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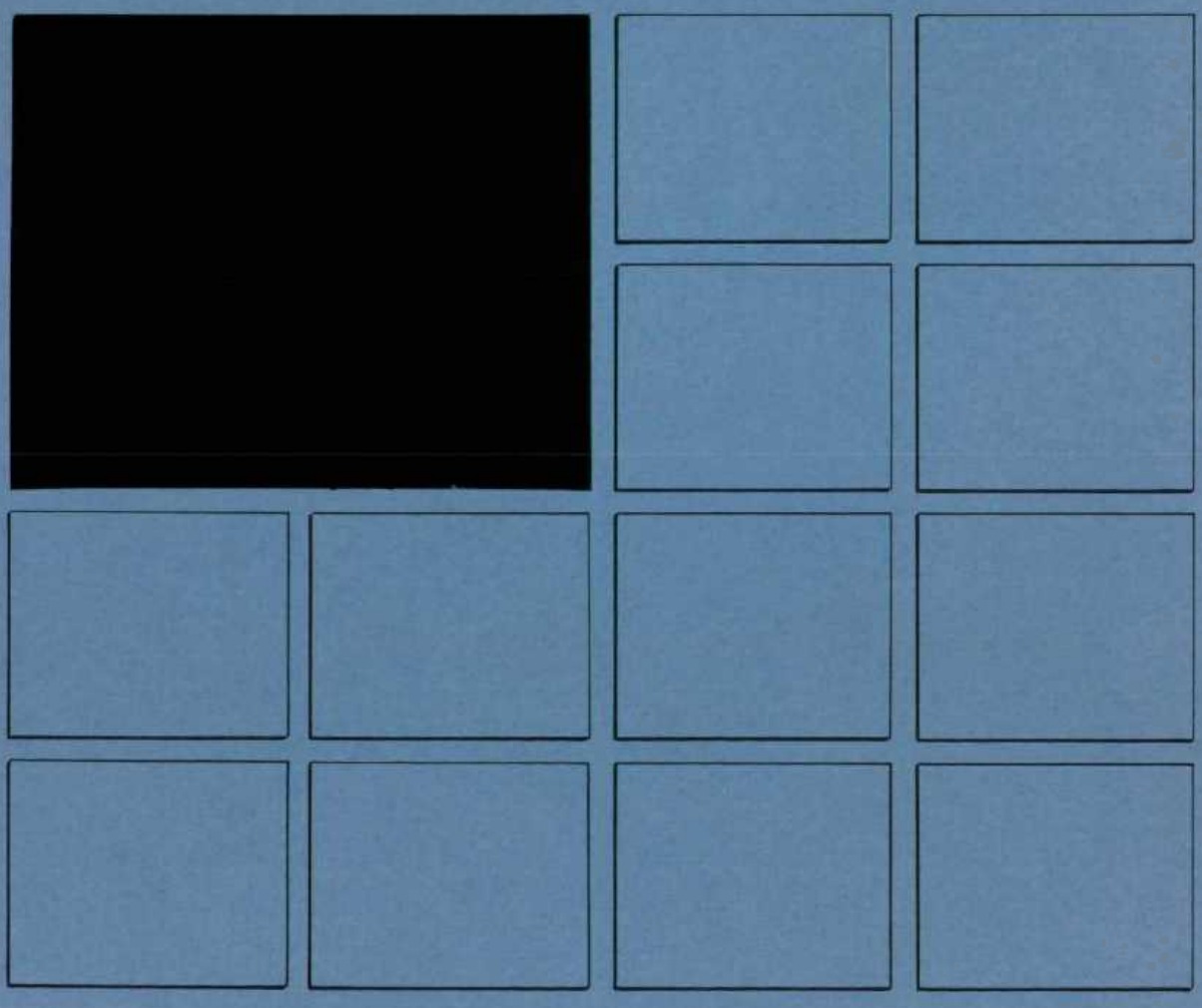

A Review of the Agrochemical Problem and Related Hydrochemical Models

by

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Total Impact of Pollutants in River Basins

SUMMARY

The overall objective of the study is to assess the sensitivity of river basins to all influences such as diffuse and discrete sources of pollutants and land use change. Needless to say this is an extremely wide brief and the first year of the research is designed to assess the feasibility of developing catchment hydrochemical models which can be used for such impact analysis.

Fortunately IH has already considerable experience developing hydrochemical models and we have recently undertaken research for water authorities, EEC and the Royal Society. River basin models have been developed to investigate pollutants such as nitrates, organic matter, heavy metals, and most recently the effects of acid deposition on catchment water quality. These models will be used to investigate the sensitivity of catchments and will be used as the basis of our feasibility study on the problems of modelling agrochemicals.

Agrochemicals are being used widely to control pests and weeds and improve crop yields. Relatively little is known about their movement into river systems and they represent a particularly important aspect of the project. This first report focuses on pesticide use and chemistry and reports the views of water authorities on the pesticide problem. A brief review of pesticide models is also presented.

CONCLUSIONS

Pesticide usage continues to increase in the U.K. so that concern with the possible effects on river catchments, especially on water quality will also continue. While the move away from the more persistent organochlorine pesticides is to be welcomed, the increasingly large quantities of OP's, pyrethroids and carbamates being applied need careful investigation with regard to their possible residue levels to be found in British rivers. Herbicides probably represent the area of most concern since their total applications dominate pesticide usage in the U.K., aerially and quantitatively.

Many factors influence the behaviour and fate of pesticides after contact with soil, including such factors as adsorption, leaching, volatilisation, erosion, microbial degradation, chemical degradation and

hydrolysis. All of the above are in part dependent on soil characteristics as well as the chemical characteristics of the pesticide. Moreover, soil erosion in agricultural areas is a major process contributing pesticides to the aquatic environment. Other sources, however, include industrial and sewage effluent and accidental spillages. All of these factors and sources need to be taken into consideration in any general study of pesticides in catchments, and in any modelling exercise.

More specifically with regard to pesticides in rivers, the present E.E.C. drinking water standards appear hopelessly misguided and open to disregard since a global standard of 0.5 ug/l for the total pesticides present takes no account of the toxic nature of individual compounds.

Recent studies both in Australia and North America, meanwhile, seem to indicate that the actual losses of pesticide rarely exceed 5% of the total, applied, and as such are not alarming. However, what is of concern is the nature of the individual pesticide concentrations reaching rivers and their possible toxic effects on aquatic fauna. Clearly, storms following recent applications of pesticides represent the main period of concern since the changeover to less persistent pesticides.

The present water authority perspective on the possible pollution problems represented by pesticides varies. Thames W.A. experience "apparent" problems with the herbicides atrazine and simazine in relationto the levels present in supply waters. Yorkshire W.A., however, experience more urgent problems based on the industrial discharges of lindane in particular, from textiles maanufacturers, while Anglian W.A. have some evidence of elevated atrazine levels, probably due to indiscriminate urban usage.

Finally, with regard to the possibility of modelling pesticide movement within catchments, work in the U.S. suggests its feasilbility. Certainly, the ARM and CREAM models offer good examples, although they both have obvious limitations. All such models require hydrology, erosion and chemical components, if they are to successfully model pesticide losses. Data inputs to them also require in many instances, detailed field observations and careful calibration and validation. Such procedures would thus also be necessary for any model derived by the authors for the British context. It is hoped that the feasibility of designing such a model can be fully assessed by the end of the present contract.

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1.1 Introduction

The use of toxic chemicals as the principal weapon against pest and disease attack, and against weeds is commonly regarded as one of the most worrying developments in modern agriculture (DOE, 1979). The quantities of chemicals used continues to rise, as will be seen later, hence this concern continues. In the context of this report, the word "pesticides" is used in the generic sense and includes insecticides, fungicides, herbicides, and other categories of compounds used to kill pest. The development of modern pesticides, while undeniably a triumph in science and technology has not been without its problems (McEwen and Stephenson, 1979). Problems such as resistance, persistence and damage to non-target organisms, for example. These and others will be investigated in this report in relation to their effects upon river water quality.

Today more than 1000 pesticide chemicals are in common use around the world, of which more than 250 are commonly used in agriculture (Ware, 1983). Only a few of these persist for more than a few weeks or at most months in soil or water, and of those that do most are the organochlorine insecticides, which include aldrin, dieldrin, chlordane, dicofol, endosulfan, endrin, lindane, DDT, heptachlor and toxaphene (Edwards, 1973).

During the 1950's and 1960's reports of large residues of these organochlorine pesticides in soils, and small amounts in water and in stream sediments, began to appear in the literature (Edwards, 1973). These discoveries began to cause concern about their long-term ecological effects and has since resulted in a move away from the use of these more persistent pesticides, towards an increasing use of less persistent organophosphorous and more recently, pyrethroid pesticides; a trend witnessed throughout the developed world at least (DOE, 1979; Ware, 1983; Garman and Sutherland, 1983).

Lastly, although pesticides are chiefly used in agriculture, they are also found elsewhere in homes and gardens, in industry, and in public health. These non-agricultural uses have been investigated by the Department of the Environment (DOE, 1974). For example, it appears that some pesticides (e.g. dieldrin) are now used in moth-proofing and wood preservation much more than they are in agriculture.

1.2 Pesticide usage in the United Kingdom

Up to 1945, chemical control of pests in England and Wales was mostly by a very limited number of chemicals (Perring and Mellanby, 1977). At that time, few pesticides were pest specific and their selectivity was usually a matter of timing, while their use was mainly confined to high value crops such as fruit, hops, market garden and glasshouse crops.

During the second World War, the organochlorine insecticides, DDT and HCH and the translocated herbicides, 2,4 - D and MCPA were developed and in the late 1940's these became available for use in British agriculture. By 1950, 15 pesticides (apart from herbicides) were approved by the Ministry of Agriculture and Fisheries (MAFF), as seen in Table 1 (DOE, 1979). By 1955 the list included 27 pesticides (including herbicides). And in 1960 it included 47, while in 1965 it listed 98. Chemicals introduced in the 1960's included: aldrin, dieldrin, endosulfan, endrin and other organochlorine insecticides, as well as many new contact herbicides such as dinoseb, paraquat and diquat (Perring and Mellanby, 1977). The 1970 Approvals List included 163 chemicals and by 1975, 200 were listed, newcomers including: aldicarb and systemic fungicides such as carboxin.

DOE (1979), summarised the growth of approved products as formulations, for the period 1944 to 1976 (Table 2). Also, the Pesticides Survey Group of MAFF has been surveying usage of pesticides on crops in England and Wales since 1965, Sly (1977) providing a review for the period 1965 to 1974. The annual usage in terms of treated area and the area of crops grown is shown in Table 3. The estimated quantities of active ingredient used are shown in Table 4. There has been a reduction in the use of organochlorine insecticides since the first review of these persistent pesticides, but up until 1977 only endrin was deleted from the Approvals List. Most of the expansion in availability of insecticides in the 1970's has thus been of contact or organophosphorous insecticides and of carbamate insecticides and acaricides.

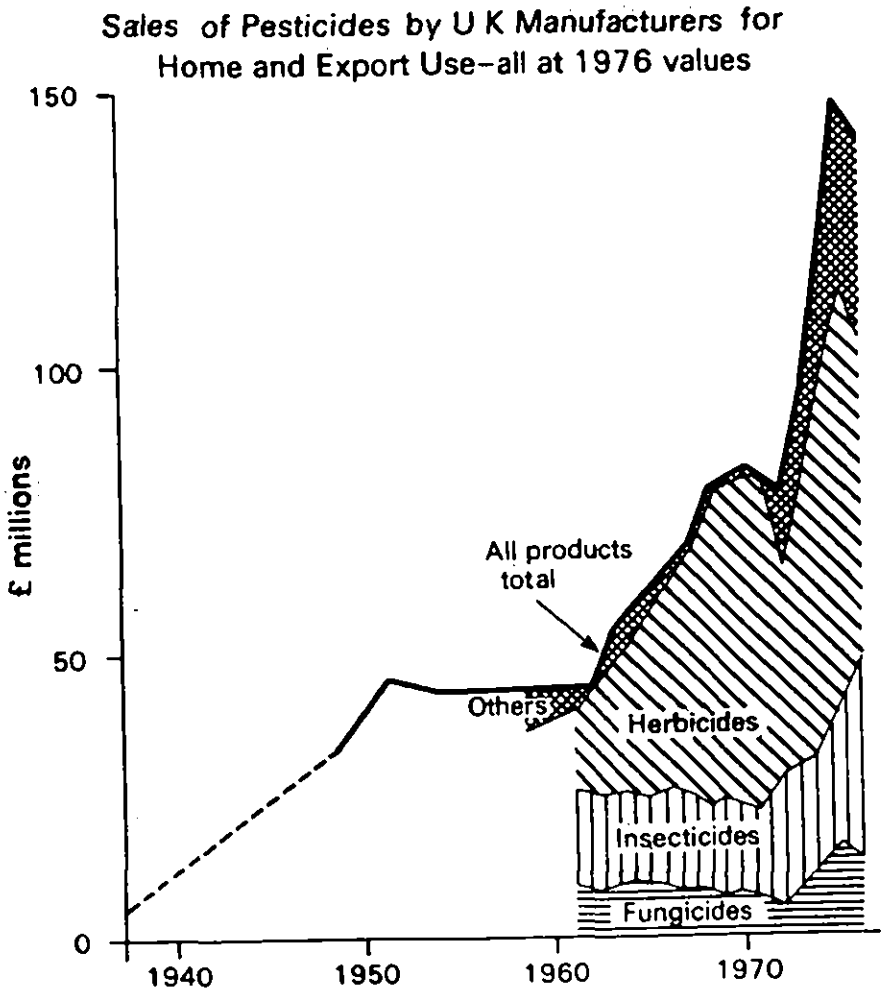


Figure 1.
Sales of Pesticides by UK Manufacturers for Home and Export use - all at 1976 values

TABLE 1

Chemicals in Approvals List of MAFF, 1950 to 1975

Chemical	Number listed					
	1950	1955	1960	1965	1970	1975
Natural insecticides	1	3	3	2	2	2
Contact organophosphorus insecticides	-	3	3	3	10	20
Systemic organophosphorus insecticides	-	-	3	2	16	15
Organochlorine insecticides	2	2	6	8	9	7
Organochlorine acaricides	-	-	4	4	4	3
Carbamate insecticides, acaricides	-	-	-	1	3	8
Other insecticides, acaricides	4	5	6	4	5	5
Systemic fungicides	-	-	-	-	4	11
Fungicides (powdery mildew)	-	-	-	3	4	5
Dithiocarbamate fungicides	-	1	1	7	10	10
General fungicides	1	1	3	5	8	13
Elemental fungicides	1	5	5	5	7	7
Mainly contact herbicides		2	3	8	14	19
Mainly soil herbicides		1	2	10	35	39
Mainly translocated herbicides		2	6	14	16	20
Soil fumigants		1	1	3	8	8
Molluscicides		1	1	1	2	2
Growth regulators				3	6	6

Source: SLY.J.M.A. in Ecological Effects of Pesticides, Academic Press London 1977, p2, (in DOE, 1979).

TABLE 2

Chemicals in Approvals List of MAFF, 1950 TO 1976

Year	Number of products
1944	63
1948	216
1952	352
1956	446
1960	532
1964	540
1968	783
1972	810
1976	819

Source: SLY.J.M.A. in Ecological Effects of Pesticides, Academic Press London 1977, p3. (in (DOE,1979).

TABLE 3

Recent data on extent of pesticide treatment of crops

England and Wales

Crop group	Year of survey	Area of crops grown (hectares)	Percentage of crops treated
Cereals	1974	3,245,845	99.5
Potatoes, sugar beet and field beans	1974	434,439	98.4
Fodder, forage and seed crops	1974	1,649,484	44.8
Vegetables	1972	221,433	94
Orchards	1973	50,355	92
Hops	1975	6,414	100
Soft fruit	1975	13,123	99
Glasshouse crops	1972	3,639	97.1
Hardy nursery stock	1971	6,500	87

(Source: Ministry pesticide survey, in DOE (1979)).

TABLE 4

Types of pesticides used in agriculture and horticulture. Estimated annual average quantities of active ingredient 1971-5 England and Wales

Pesticide group	"Spray hectares" (a)	Tonnes of active ingredient per year
Insecticides		
Organochlorine compounds	148,105	132
Organophosphorus compounds	844,011	419
Other insecticides	117,232	779
Seed treatments	3,717,621	565
Fungicides	1,896,538	2,194
Herbicides	6,020,624	15,712
Other pesticides	49,438	1,960
Total	12,645,212	(b)

(Source: Ministry pesticide surveys, in DOE (1979))

The biggest changes in fungicides involved the introduction of systemic.fungicides in the late 1960's. Their greater efficiency having led to economic control of a variety of plant diseases. Also, the number of herbicides available up to 1976 increased about 2 times, partly as a result of new chemicals with general herbicidal activity and also partly due to the increased use of chemicals to control grass weeds in cereals.

Thus, the trends in pesticide usage up to 1976 can be roughly summarised in the form of a graph of sales in the UK (Figure 1). However, it appears that, in 1976, nearly 50 per cent of sales by value were exported. While, of that sold inside the UK, nearly 90 per cent were for use in agriculture and horticulture (DOE, 1979). But, there was an upward trend in sales of pesticide reflecting increased usage and not merely increased costs (DOE, 1979). More recent data on pesticide usage for 1977 are presented in Tables 5, 6 and 7 (DOE, 1979).

What is not apparent from these tables is the declining use of organochlorine compounds in agriculture. In addition, there is evidence of a substanial increase in the use of herbicides on certain crops and a recent increase of insecticide use on cereals. Indeed, herbicides form the majority of pesticides applied and are now used on virtually all agricultural and horticultural crops grown on any scale, crops often receiving two or more applications. It has been estimated (Fryer, 1977) that the total area of agricultural land in the UK treated with herbicides is in the range of 4.2 to 5.4 million hectares.

Since 1977, Sly has published two other reviews of pesticide usage (Sly 1981 and 1985). First, for the period 1975 to 1979 (Sly, 1981) Table 8, gives a comparison of their usage on agricultural and horticultural crops. There was little overall change in usage of the organochlorines and the increased usage of organophosphorous insecticides was mostly on cereals to control aphids. The large increase in the area treated with other insecticides, acaricides and molluscicides was mostly the increased usage of pirimicarb to control cereal aphids and increased usage of aldicarb, methiocarb and the synthetic pyrethroids. There were no substantial changes in usage of seed treatments apart from the replacement of persistent aldrin or dieldrin/mercury on cereals and sugar beet with other formulations.

TABLE 5

Types of pesticides used on cereals, 1974 and 1977
Estimated quantitites of active ingredients, England and Wales

Pesticide groups	Spray hectares 1974	Spray hectares 1977	Tonnes of active ingredients 1974	Tonnes of active ingredients 1977
Insecticides				
Organochlorine compounds	0	1,000	0	1
Organophosphorus compounds	41,000	294.000	17	107
Other insecticides	5,000	272,000	1	43
Seed treatments	3,309,000	3,358,000	553	480
Fungicides	616,000	978,000	394	588
Herbicides	4,475,000	4,408,000	8,727	8,026
Other presticides	67,000	188,000	84	263
Total	8,513,000	9,499,000		

(Source: Ministry pesticide surveys)

TABLE 6

Types of pesticides used on other arable crops. *1974 and 1977 Estimated quantities of active ingredients, England and Wales

Pesticide groups	Spray hectares 1974	Spray hectares 1977	Tonnes of active ingredients 1974	Tonnes of active ingredients 1977
Insecticides				
Organochlorine compounds	30,000	40,000	22	35
Organophosphorus compounds	469,000	274.000	191	99
Other insecticides	19,000	180,000	36	416
Seed treatments	433,000	430,000	2	2
Fungicides	599,000	616,000	696	882
Herbicides	648,000	918,000	4,835	6,131
Other presticides	0	0	0	0
Total	2,198,000	2,458.000		

(Source: Ministry pesticide surveys)
*potatoes, sugar beet, field beans, rape, mustard.
Source: DOE (1979)

TABLE 7

Frequency of pesticide treatment*

Estimated percentage of planted area of arable crops receiving particular total numbers of annual treatments

England and Wales, 1977

	Area planted (hectares)	Number of treatments received			
		0	1-3	4-6	7-more
Cereals	3,209,329	1%	55%	42%	2%
Other arable crops	476,261	1%	43%	46%	10%

(Source: Ministry of pesticide surveys)
*Including seed treatment

TABLE 8 Estimated annual usage of pesticides in agriculture and horticulture in England and Wales, 1971-9174 and 1975-1979 (spary hectares and tonnes of active ingradients)

Pesticide	1971-1974		1975-1979	
	Spray hectares	Tonnes	Spray hectares	Tonnes
OC insecticides, acaricides	148,000	131	146,000	166
OP insecticides	845,000	430	975,000	534
Other insecticides, acaricides, molluscicides	93,000	1,286	597,000	907
Seed Treatments	3,718,000	565	3,753,000	591
Fungicides	1,895,000	2,400	2,253,000	2,336
Herbicides, defoliants	6,003,000	15,250	7,868,000	19,925
Other pesticides	81,000		203,000	1,038

*including chemicals for burning-off

Source: Sly (1981)

However, there was an overall increase in usage of fungicides mainly due to a large increase in usage of systemic fungicides. The apparent large increase in usage of herbicides is mainly accounted for by the 1.8 m ha of grassland which were treated in 1979, with no comparable data avilable for the period 1971-1975. But there was an increase in the usage of total herbicides such as paraquat and glyphosate, mostly for stubble clearing, and of herbicides for the control of grass weeds in cereals.

Usage of pesticides on each group of crops (1975-1979) is summarised in Table 9 (Sly, 1981). Other arable crops consisted mostly of potatoes, sugar beet, field beans, mustard and rape grown as seed crops. Although not included in Table 9, the comparative figure for usage in Forestry in 1978 is 0.04 applications. Overall usage varied considerably and is shown below:

Crop Group	Mean number of pesticide applications
Fodder/forage crops (mostly grass)	0.4
Cereals	3.0
Vegetables	3.9
Other arable crops	4.8
Hardy nursery stock	6.1
Glasshouse crops	8.1
Soft fruit	8.7
Orchards	17.1
Hops	23.4
* Forestry	0.04

* 1978 only

In terms of spray area, the most extensive usage was of seed treatments and translocated herbicides (both mainly to cereals). The largest tonnages of active ingredients were dithiocarbamate fungicides (mostly on potatoes), herbicides and sulphuric acid used at high rates of active ingredient per acre on about one-fifth of main crop potatoes.

TABLE 9 Annual usage of pesticides in agriculture and horticulture, England and Wales, 1975-1979 spray hectares and tonnes of active ingredients

	Soft fruit 1975		Glasshouses 1976		Hardy nursery stock 1976		Vegetables 1977		Cereals 1977	
	ha				ha					
Insecticides, molluscicides, acaricides										
Organochlorines	15,902	14.58	3,075	3.01	2,926	3.62	41,378	40.07	813	1.02
Contact organophosphates	4,875	5.76	4,310	6.06	1,792	2.02	119,511	109.46	6,551	4.20
Systemtic organophosphates	10,275	3.57	1,862	0.72	7,937	2.30	174,663	104.60	287,476	121.84
Carbamates	2,035	1.22	3,253	6.53	982	1.40	30,406	36.44	269,082	73.91
Others	1,267	39.85	4,773	9.98	312	17.87	301	0.24	3,011	2.83
Total	34,354	64.98	17,273	26.30	13,949	27.21	366,159	290.81	566,933	203.80
Insecticide/fungicide mixtures			738	0.83	3	trace				
Seed Treatments			7	trace	3	trace	161,671	64.60	3,272,918	496.88
Fungicides										
Systemic	12,763	8.19	5,068	7.42	4,505	2.85	24,277	16.05	910,171	461.67
Mainly against powdery mildews	10,991	13.72	808	0.56	3,336	2.70	194	0.10	2,212	1.66
Dithiocarbamates	7,851	20.74	13,594	55.03	1,738	2.93	9,556	13.82	28,438	49.19
Others	19,459	38.23	2,392	33.23	2,460	5.57	7,062	6.00	36,004	56.01
Total	51,064	80.88	21,862	96.24	12,039	15.05	41,089	35.97	976,825	568.53
Herbicides, defoliants										
Mainly contact	5,791	5.01	135	0.16	3,451	3.46	118,110	280.05	542,560	811.57
Mainly soil-acting	19,530	70.17	447	1.05	7,369	17.26	262,149	515,81	588,370	1,203.77
Mainly translocated	3,825	9.30	1	trace	764	2.23	13,087	17.98	3,455,691	5,566.79
Sulphuric acid							2,048	345.29		
Tar oil										
Total	29,146	84,48	583	1.21	11,584	22.95	395,394	1,159,13	4,576,621	7,582.13
Growth regulators			904	1.53	42	trace	2,981	10,43	188,136	238.93
Soil sterilants, fumigants	17	trace	2,013	610.22	153	47.65	203	79.84		
Total area treated	114,581	230,34	43,380	736.33	37,773	112.86	967,497	1,640.78	9,581,433	9,090.27
Area grown	13,123		5,350		6,156		250,702		3,209,331	

Source: Sly (1981)

TABLE 9 Annual usage of pesticides in agriculture and horticulture, England and Wales, 1975-1979 spray hectares and tonnes of active ingredients
Continued

	Other arable crops 1977		Forfer/forage 1979		Orchards 1979		Hops 1979		Total	
	ha		ha		ha		ha		ha	
Insecticides, molluscicides, acaricides										
Organochlorines	40,061	51.07	3,728	5.81	21,551	23.26	16,918	23.42	146,252	165.85
Contact organophosphates	9,688	6.14	2,341	2.34	30,305	26.72	10,212	10.20	189,585	172.90
Systemtic organophosphates	264,709	106.68	1,512	0.26	32,161	12.72	4,923	8.49	758,518	361.18
Carbamates	173,740	158.63	6,267	1.36	13,183	23.36	10,586	12.15	509,534	314.00
Others	6,009	3.37	4,913	4.57	63,270	513.58	3,539	0.52	87,395	592.81
Total	494,207	325.89	18,761	14.34	160,470	598.64	46,178	54.78	1,718,284	1,606.75
Insecticide/fungicide mixtures									741	0.83
Seed Treatments	235,084	8.87	82,974	20.57					3,752,657	590.92
Fungicides										
Systemic										
Mainly against powdery mildews	8,985	5.58	23,383	9.69	69,105	33.66	26,460	5.51	1,084,717	550.62
Dithiocarbamates	.	.	.	.	172,077	128.18	3,027	1.34	192,645	148.26
Others	513,526	770.81	2,329	4.34	12,742	29.46	20,657	58.63	610.431	1,005.94
Total	93,861	56.39			187,707	374.01	16,206	61.79	365,151	631.23
	616,372	832.78	25,712	14.03	441,631	565.31	66,350	127,27	2,252,944	2,336.05
Herbicides, defoliants										
Mainly contact	297,890	348.17	112,621	39.03	16,654	6.84	8,356	11.02	1,105,568	1,505.31
Mainly soil-acting	501,799	890.66	123,439	181.09	31,481	46.80	3,983	7.12	1,538,567	2,933.73
Mainly translocated	85,343	148.66	1,557,032	842.14	77,682	116.05	1,761	3.25	5,185,186	6,706.38
Sulphuric acid	33,081	8,171,01					.	.	35,129	8,516.30
Tar oil							5,977	265.58	5,977	265.58
Total	918,113	9,558.50	1,793,092	1,062.26	125,817	169.69	20,077	286.95	7,870,427	19,927.31
Growth regulators					7,770	3.65	803	trace	200,636	254.54
Soil sterilants, fumigants	208	45.76							2,594	783.47
Total area treated	2,263,984	10,771.80	1,920,539	1,111.20	735.688	1,337.29	133,408	469.00	15,798,203	25,499.87
Area grown	476,117		5,327,950		42.916		5,706		9,337,351	

Source: Sly (1981)

The most extensive areas treated with insecticides, acaricides and molluscicides were with demeton-s-methyl and dimethoate to most crops, and pirimicarb especially upon cereals. About two-thirds of all seed treatments included mercury, about 80 percent of cereals and all sugar beet seed being so treated. Also large quantities of ethirimol and HCH/mercury were used as seed treatment. The most extensive areas treated with fungicides were with tridemorph, carbendazim, "Dithane" (either mancozeb or zineb), and benomyl. Apart from Dithane (used mostly on potatoes) these fungicides are all systemic. The systemics were mostly applied to cereals, the dithio carbamates to potatoes and captan and sulphur to fruit and hops. In terms of quantity of active ingredients, usage of eight fungicides exceeded 100 tonnes. These were mancozeb, tridemorph, captan, zineb, sulphur, maneb, carbendazim/maneb and propineb. Lastly the usage of herbicides is complicated because many of them are formulated as mixtures, but the most widely used active ingredients were dicamba, dichlorprop and mecoprop, mostly alone. Similarly, the quantities of active ingredients are obscured by mixtures but extensive quantities of most of the above were used.

As nearly 400 pesticides or formulated mixtures of pesticides were recorded during 1975-1979 it is not feasible to compare the changes in use of each of them. The most important are shown in Table 10 (Sly, 1981). Of the insecticides, there were very large increases in usage of aldicarb, pirimicarb and dimethoate on most crops and a large increase in triazophos usage, mostly on brassicas. The increased usage of methiocarb was mostly on arable crops. There was also evidence, towards the end of the survey of a large scale usage of synthetic pyrethroids (especially permethrin and decamethrin). Cereal seed treatments showed the withdrawal of aldrin/mercury and dieldrin/mercury and an increase in usage of HCH/mercury in their stead. On sugar beet, dieldrin/mercury has been replaced by methiocarb/mercury.

Changes in usage of fungicides are marked by large increases in systemic fungicides including the introduction of new chemicals such as triadimefon. The reduced use of maneb and fentin acetate maneb on potatoes has been matched by increased usage of mancozeb and of captafol. Lastly, several herbicides have shown increased usage, notably paraquat (and glyphosate) for total weed control, benazolin mixtures for broad leaved weed control in cereals, flamprop-isopryl, isoproturon and difenzoquat for control of grass weeds and trifluralin on brassicas.

TABLE 10 The more important usage of pesticides in 1971-1974 and 1975-1979 (spray area '000 ha) (Sly, 1981)

Pesticide	Usage in 1971-1974	Usage in 1975-1979
INSECTICIDES, ACARICIDES, NEMATICIDES, MOLLUSCICIDES		
DDT	62	59
Triazophos	3	50
Demeton-S-methyl	337	408
Dimethoate	115	224
Aldicarb	3	89
Pirmicarb	29	316
SEED TREATMENTS		
Aldrin/mercury	22	0
Dieldrin/mercury	212	0
Chlorfenvinphs/mercury	106	73
Ethirimol	436	477
HCH/captan	42	99
HCH/mercury (single rate)	1,247	780
HCH/mercury (double rate)	144	173
Mercury	1,322	1,472
Methiocarb/mercury	10	203
FUNGICIDES		
Benomyl	45	120
Carbendazim	2	213
Triadimefon	0	121
Tridemorph	422	367
Dinocap	131	54
Mancozeb	242	293
Maneb	153	80
Dithian	95	71
Fentin acetate/maneb	133	64
HERBICIDES		
Bromoxynil/ioxynil/dichlorprop	100	179
Paraquat	229	379
Phenmedipham	114	155
Isoproturon	2	157
Tri-allate, di-allate	377	309
Barban	257	177
Benazolin mixtures	9	216
Benzoylprop-ethyl	164	220
2,4-D	210	193
Dicamba/MCPA	242	12
Dicamba/Mecoprop/MCPA	290	577
Dichlorprop	175	155
Dichlorprop/MCPA	162	29
Digenzoquat	7	254
Flamprop-isopropyl	1	108
MCPA	990	950
Mecoprop	710	644
2,4,5-T(alone)	6*	173
2,3,6-TBA/Dicamba/MCPA/mecoprop	200	269
Trifluralin	16	80
OTHER CHEMICALS		
Chlormequat	42	188
Maleic hydrazide	0.6	3
Methyl bromide	0.2	0.6

More recently, a review of pesticide usage for the period 1980 to 1983 has been published (Sly, 1985). A summary of usage on all crops in the periods 1971-74, 1975-79 and 1980-83 is shown in Table 11. The quantity of the organochlorine insecticides used in 1980-83 fell compared with 1975-79 although the area treated increased, mainly due to the usage of HCH on the greatly increased area of oilseed rape. The annual usage of DDT continued to drop from about 70 tonnes to about 34 tonnes in 1980-83, 31000 ha being treated compared with 59000 ha in 1975-79. There was little change in the usage of organophosphates. The use of carbamates increased dramatically mainly due to methiocarb being used to control slugs in cereals. There was a large increase in usage of pyrethroids on most crops, applied at low rate of active ingredients. The drop in quantities of applied seed treatments since 1979 arose from the replacement of ethirimol as a cereal seed treatment with other sytemic fungicides applied at much lower rates of active ingredients. There was a large overall increase in usage of fungicides, mostly from the increased usage of foliar-applied systemic fungicides to cereals. Most of the increased usage of herbicides meanwhile, was on cereals and other arable crops, although the greater area of grass included in the surveys in 1980-83 increased the treated area of grass. Expanded summaries of usage in 1980-83 are shown in Table 12 (treated hectares) and Table 13 (tonnes of active ingredients).

1.3 The chemistry of some commonly applied pesticides

There are several general classes of pesticides, as shown in the above tables. The most commonly used being the organochlorine, organophosphorous, carbamates and more recently synthetic pyrethroids. These can perhaps best be summarised by reference to some examples of the most commonly applied insecticides, fungicides and herbicides available in the U.K.

a) Insecticides

(i) Organochlorines

The organochlorines are insecticides that contain carbon, chlorine and hydrogen, the chlorine being substituted at various points on either a chain or ring structure of hydrocarbons. As a general rule, it has been shown that the more chlorine substitution, the better the chemical is as a pesticide, and also the more resistant it is to degradation. However,

TABLE 11 Estimated annual usage of pesticides oncrops in agriculture and horticulture in England and Wales, 1971-74, 1975-79 and 1980-83 (treated hectares and tonnes of active ingredients)

Pesticide	1971-74		1975-79		1980-83	
	Treated hectares	Tonnes	Treated hectares	Tonnes	Treated hectares	Tonnes
Organochlorines, insecticides, acaricides	148000	131	146000	166	160000	130
Organophosphate insecticides	845800	430	975000	534	923000	591
Pyrethroids	1000	<1	41000	2	172000	8
Other insecticides, acaricides, molluscicides	92000	1286	556000	905	956000	664
Seed treatments	3718000	565	3753000	591	3883000	301
Fungicides	1895000	2400	2253000	2336	6715000	4341
Herbicides, defoliants*	6003000	15250	7868000	19925	12402000	26340
Other pesticides	81000	2000	203000	1038	801000	3138
Area of crops and grass	563100[a]		9322000		10511000	

* including chemicals for burning-off

a permanent grass was not included in 1971-1974

TABLE 12 Total annual usage of pesticides 1980-83 - treated area - hectares (Sly, 1985)

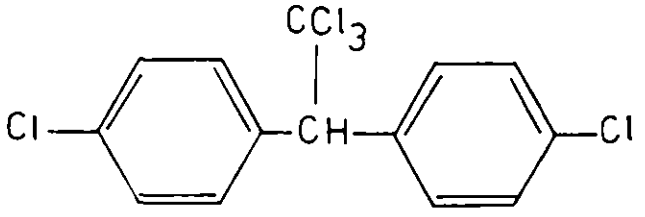
Chemicals	Soft fruit	Pro-tected crops	Hardy nursery stock	Vege-tables, bulbs	Cereal	Other arable	Grass	Orchard	Hops	Total agric, hort
	1980	1981/2	1981	1981/2	1982	1982	1982	1983	1983	1980-83
Organochlorines	16576	2093	2592	32350	9153	85858	128	6091	5382	160223
Contact organophosphates	5397	2606	2244	89092	56577	80234	723	27093	1848	265814
Systemic organophosphates	9366	2105	6670	164401	315898	123534	1197	29108	5378	657657
Carbamates	2616	3253	1504	38931	550443	295635	2181	23766	1987	920316
Pyrethroids	1907	3069	1700	25130	74901	3665	0	33972	27502	171846
Other ins/acar/moll	5351	2653	1021	172	78406	9485	4914	33333	681	136016
Total ins/acar/moll	41213	15779	15731	350076	1085378	598411	9143	153363	42778	2311872
Total : seed treatments	0	9	0	124254	3189459	565193	4441	0	0	3883356
Total ins/fung mixtures	0	264	28	0	0	0	0	0	0	292
Systemic fungs	23496	4416	9184	26359	4702753	105382	19412	157743	32128	5080873
Systemic/dithio.	53	1301	525	5798	252026	170694	7007	22	335	432761
Powdery mildew fungs	5802	811	6311	17	1890	0	0	78739	8874	102444
Dithiocarbamates	8576	3728	1909	13757	149805	233218	3004	4473	7555	426025
General fungicides	34705	10245	2950	13417	128309	55560	0	162645	2358	410189
Elemental fungs	3066	194	282	3080	11969	220322	0	14840	9185	262938
Total fungicides	75698	20695	21161	62428	5246752	785176	24423	418462	60435	6715230
Total herbicides	41274	850	19610	334100	7395138	1672082	2788256	127556	23390	12402256
Growth regulators	2	797	358	3456	770173	11433	0	8910	144	795273
Soil sterilants,disinfectants	70	2308	221	200	0	3122	0	0	3	5924
Total : other chemicals	72	3105	579	3656	770173	14555	0	8910	147	801197
Total treated area	158257	40702	57109	874514	17686900	3635417	2826263	708291	126750	26114203
Area grown	15105	4447	6003	194923	3444486	661287	6143427	35443	5912	10511033

TABLE 13 Total annual usage of pesticides 1980-83 - tonnes of active ingredients (Sly, 1985)

Chemicals	Soft fruit 1980	Protected crops 1981/2	Hardy nursery stock 1981	Vege tables, bulbs 1981/2	Cereal 1982	Other arable 1982	Grass 1982	Orchard 1983	Hops 1983	Total agric, hort, 1980-83
Organochlorines	15.59	1.76	3.10	30.09	12.86	55.82	0.04	5.91	5.32	130.49
Contact organophosphates	4.70	15.37	2.62	134.08	48.87	43.68	0.54	21.23	1.40	272.49
Systemic	4.83	1.22	3.32	107.62	102.42	64.88	0.41	17.30	16.78	318.78
Carbamates	1.43	3.06	1.03	33.61	115.65	271.95	0.48	15.66	1.08	443.95
Pyrethroids	0.13	0.92	0.08	0.84	3.29	0.15	0.00	1.42	0.74	7.57
Other ins/aca/moll	20.76	5.91	2.19	0.16	70.57	5.94	4.42	110.34	0.44	220.73
Total ins/acar/moll	47.44	28.24	12.34	306.40	353.66	442.42	5.89	171.86	25.76	1394.01
Total : seed treatments	0.00	0.00	0.00	32.94	234.95	33.04	0.07	0.00	0.00	301.00
Total : ins.fung mixture	0.00	3.44	0.03	0.00	0.00	0.00	0.00	0.00	0.00	3.47
Systemic fungs	9.55	6.29	4.57	12.42	1459.17	35.35	5.69	38.81	14.81	1586.66
Systemic/dithio.	0.04	1.16	0.79	6.52	511.99	194.64	2.16	0.02	0.29	717.61
Powdery mildew fungs	5.62	0.65	4.95	0.00	1.06	0.00	0.00	101.95	3.72	117.95
Dithiocarbamates	19.95	11.52	5.21	22.34	207.43	332.83	9.37	11.61	19.79	640.05
General fungicides	59.74	56.80	4.69	13.88	162.53	50.43	0.00	234.86	4.63	587.56
Elemental fungs	8.30	1.74	0.61	2.20	57.45	529.69	0.00	53.65	37.19	690.83
Total fungicides	103.20	78.16	20.82	57.36	2399.63	1142.94	17.22	440.90	80.43	4340.66
Total : herbicides	68.84	2.10	33.03	743.25	12626.95	11653.54	974.27	180.71	77.50	26360.12
Growth regulators	0.00	0.33	0.18	12.20	1093.94	15.33	0.00	6.38	0.04	1128.40
Soil sterilants,disinfectants	25.39	452.56	76.94	7.82	0.00	1447.02	0.00	0.00	0.15	2009.88
Total : other chemicals	25.39	452.89	77.12	20.02	1093.94	1462.35	0.00	6.38	0.19	3138.28
Total tonnes	244.87	564.83	143.34	1159.97	16709.12	14734.29	997.45	799.85	183.88	35537.52

these cause severe water quality problems because of their very slow degradation rates.

DDT is undoubtedly the most famous and infamous of the organochlorines. The U.S.E.P.A. cancelled all uses of DDT in 1973 (Ware, 1983) and the DOE has encouraged its demise in recent years due to its long term persistence in soils and its accumulation in food chains. The chemical structure for DDT is presented below:

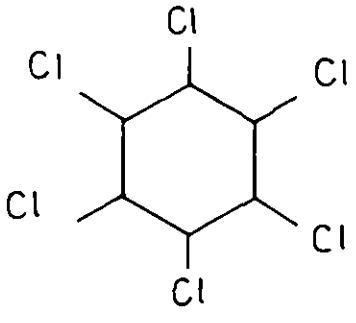


The chemical is highly persistent due to its chemical stability. Second, DDT's solubility in water is only about 6 ppb of water, i.e. probably the most water-insoluble compound ever synthesized. However, it is quite soluble in fatty tissue, and, as a consequence of its resistance to metabolism, it is readily stored in the fatty tissue of any animal ingesting DDT alone or DDT dissolved in the food it eats, even when it is part of another animal.

HCH (Hexachlorocyclohexane)

HCH is made by chlorinating benzene, which results in a product made up of several isomers, that is, molecules containing the same kinds and number of atoms but differing in the internal arrangement of those atoms. HCH has five isomers, alpha, beta, gamma, delta and epsilon. But, only the gamma isomer has insecticidal properties. Since the gamma isomer is the only active ingredient, methods were developed to manufacture lindane, a product containing 99 percent gamma isomer, which is effective against most insects, but also quite expensive, making it impractical for crop use.

The structure of HCH is given below:

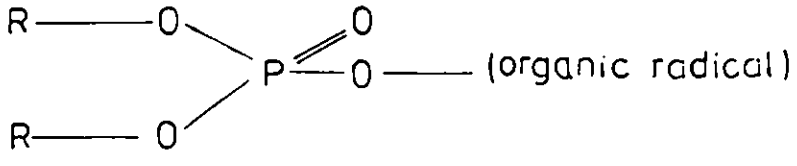


Cyclodienes

Generally, the cyclodienes are persistent and are stable in soil and relatively stable to the ultraviolet action of sunlight. Consequently, they have been used in greatest quantity as soil insecticides (especially chlordane, heptachlor, aldrin and dieldrin). Because of their persistence, their use on crops was restricted; undesirable residues remaining beyond the time for harvest (Ware, 1983). Most agricultural uses of these were cancelled by the EPA between 1975 and 1980, and their use has since been discouraged in the U.K. due to their persistence. Also, the cyvlodienes are highly toxic to fish (Ware, 1983) because when they are introduced into water the fish continually respire and ingest any toxic compound contained in their aquatic environment.

(ii) Organophosphates

The chemically unstable organophosphate (OP) insecticides have virtually replaced the persistent organochlorine compounds, especially in home and garden usage. As the name implies, these compounds are organically complexed phosphorous molecules which generally have the structure shown below:



These compounds are normally easily hydrolized and are therefore somewhat easily degraded. However, almost all of the compounds in this group have a very high toxicity in mammals.

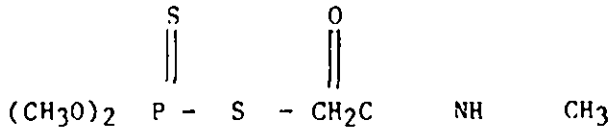
Thus the OPs have two distinctive features. First, they are generally much more toxic to vertebrates than are the OCs, and, second, they are chemically unstable or non persistent. They are divided into three groups - the aliphatic, phenyl, and heterocyclic derivatives.

Aliphatic Derivatives

The term aliphatic means "carbon chain" and the linear arrangement of carbon atoms differentiate them from ring or cyclic structures. All of these are simple phosphoric acid derivatives bearing short carbon chains.

Contained among the aliphatic derivatives are several plant systemics including the commonly used dimethoate shown below:

DIMETHOATE (Cygon)



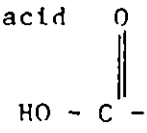
Phenyl Derivatives

When the benzene ring is attached to other groups it is referred to as phenyl. The phenyl OPs contain a benzene ring with one of the ring hydrogens displaced by attachment to the phosphorous moiety and others frequently displaced by Cl, NO_2, CH_3, CN or S. The phenyl OPs are generally more stable than the aliphatic OPs; consequently their residues are longer lasting.

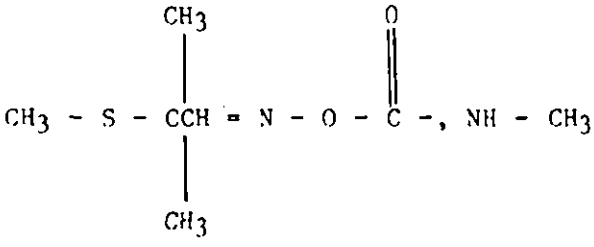
Heterocyclic Derivatives

The term heterocyclic means that the ring structures are composed of different or unlike atoms. In a heterocyclic compound, for example, one or more of the carbon atoms is displaced by oxygen, nitrogen or sulphur, and the ring may have three, five or six atoms. Generally they have longer-lasting residues than many of the aliphatic or phenyl derivatives. Also, because of the complexity of their molecular structures, their breakdown products (metabolites) are frequently many, making their residues sometimes difficult to measure in the laboratory.

(iii) Carbamates

Carbamates are derivatives of carbonic acid  and are broad-spectrum in effectiveness. Several of the carbamates are plant systemics, indicating that they have a high water solubility, which allows them to be taken into the roots or leaves. They are also not readily metabolized by the plants. For example, aldicarb, (shown below has distinct systemic characteristics.

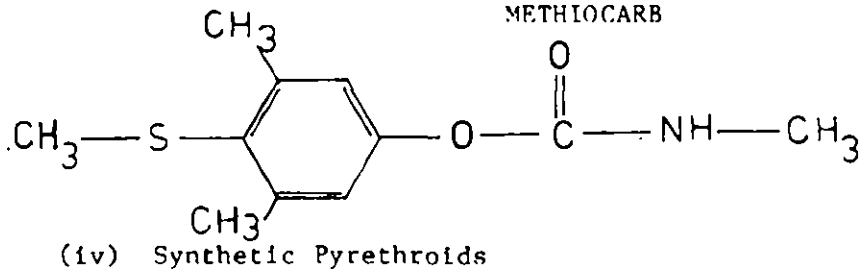
ALDICARB (Temik)



Aldicarb is also used as a soil insecticide and under rare circumstances has been detected in shallow groundwater following certain uses (Ware, 1983).

Methiocarb is another commonly used carbamate (shown below) and is effective against foliage- and fruit- eating insects, as well as against molluscs. It is also registered as a bird repellant for cherries and as a seed dressing.

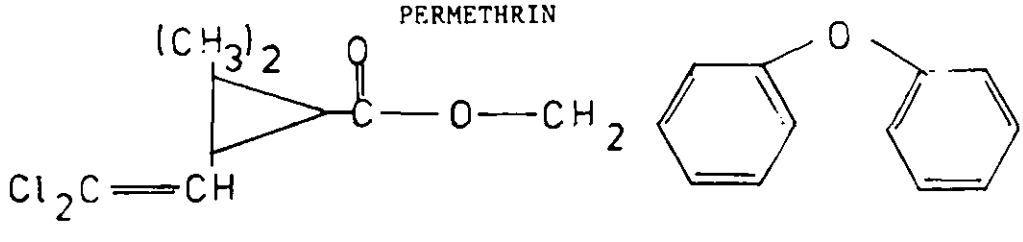
METHIOCARB



(iv) Synthetic Pyrethroids

These are very stable in sunlight and are generally effective against most agricultural pests when used at a low rate of 0.11 to 0.23 kg/ha. Examples are permethrin and decamethin. Permethrin (shown below) appeared in 1973:

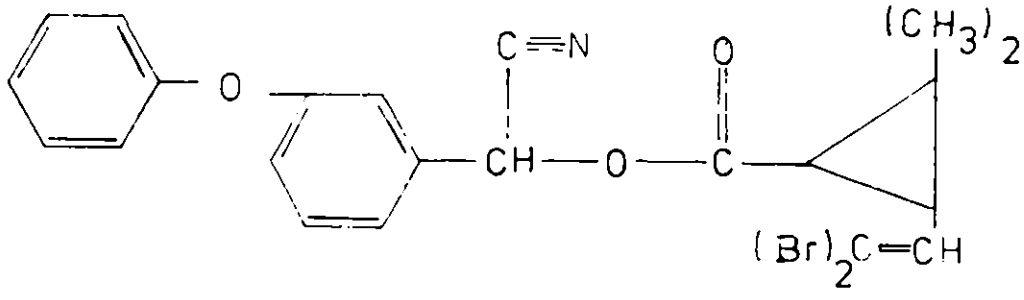
PERMETHRIN



One of the first agricultural pyrethroids because of its exceptional insectidal activity (0.11 kg AI/ha) and its photostability, lasting four to seven days on crop foliage as effective residues.

A more recent generation of pyrethoids, includes decamethrin, with rates of application reduced to one-tenth of the above (i.e. 0.01 to 0.06 kg AI/ha). This is fairly phenomenal compared to the rate of 1.1 to 2.3 kg AI/ha required of the OP, carbamate and OC insecticides. Decamethrin, is shown below:

DECAMETHRIN (Decis)



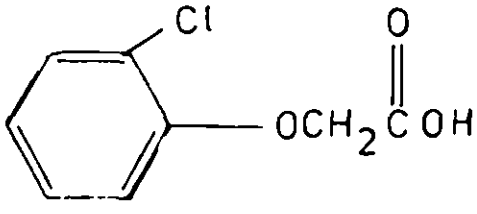
All of these insecticides are photostable, providing long residual effectiveness in the field at low applications.

b) Organic Herbicides

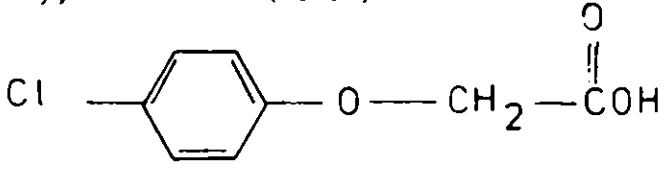
(i) *Phenoxyaliphatic Acids*

An organic herbicide introduced in 1944, later to be known as 2,4-D, was the first of these herbicides. These are highly selective for broad leaf weeds and are translocated throughout the plant. Several compounds belong to this group, of which 2,4-D, MCPA and the notorious 2,4,5-T are the most familiar.

All three of the above have been used for years in very large volume worldwide with no adverse effects on human or animal health. 2,4-D (shown below)



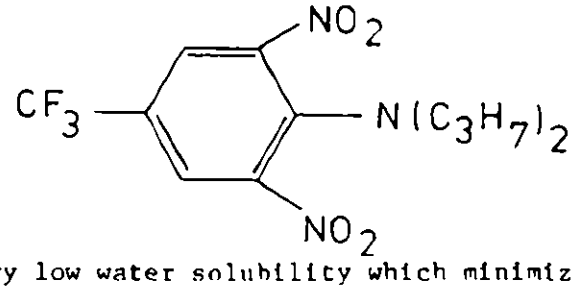
continues to be extremely useful. In agriculture it is used on cereal and grain crops for the control of broad-leaf weeds and on paths and in forestry, as is MCPA (below):



(ii) Nitroanilines

These are probably the most heavily used group of herbicides in agriculture. They are used almost exclusively as soil-incorporated pre-emergence selective herbicide in many field crops. A commonly used example in the U.K. is Trifluralin (shown below):

TRIFLURALIN (Treflan)



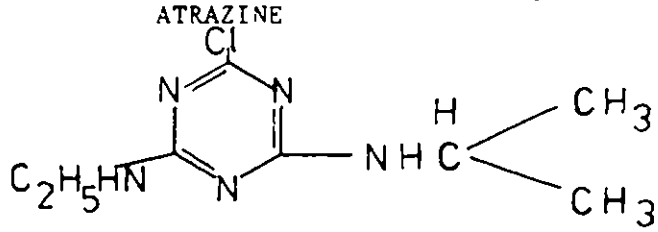
This has a very low water solubility which minimizes leaching and movement from the target.

(iii) Heterocyclic Nitrogens

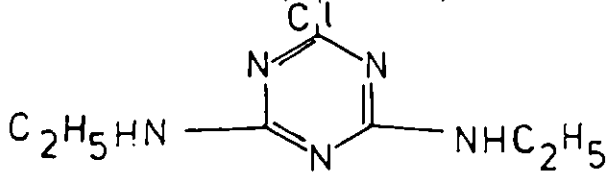
The triazines, which are six-member rings containing three nitrogens, and azine (a nitrogen containing ring) make up this group.

Probably the most familiar group of heterocyclic nitrogens, because of their heavy use are the triazines, which are strong inhibitors of photosynthesis. Their selectivity depends on the ability of tolerant plants to degrade or metabolize the parent compound (the susceptible plants do not). Triazines are applied to the soil primarily for their post-emergence activity. Two common ones are illustrated below:

ATRAZINE



SIMAZINE (Aquazine)

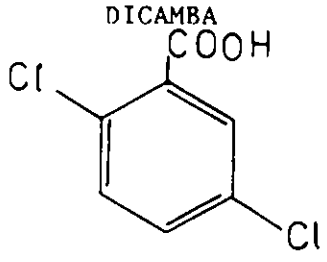


They are used in greatest quantity in corn production and nonselectively on industrial sites.

(iv) Aryaliphatic Acids

These are aryls, or six-member rings attached to aliphatic acids. For example, dicamba (below) is applied to the soil against germinating seeds and seedlings.

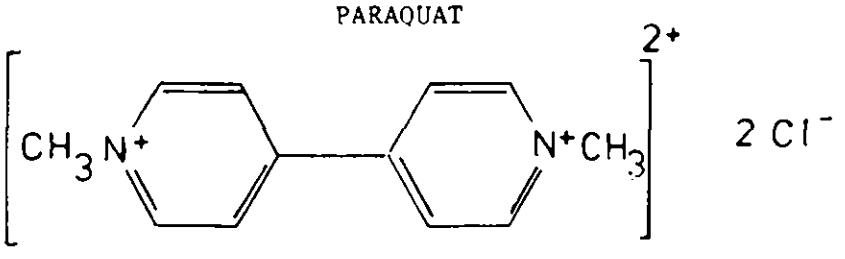
DICAMBA



(v) Bipyridyliums

There are two important herbicides in this group, diquat and paraquat. Both are contact herbicides that damage plant tissues quickly. Rapid wilting and dessication occur within hours. Neither is active in soils and in the U.S. they are only available to professional weed control specialists (Ware, 1983). Paraquat is more commonly used in the U.K. (Sly, 1985) and is shown below:

PARAQUAT

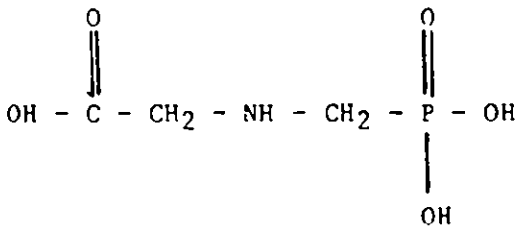


Because all the leaves drop off, paraquat is considered a defoliant and is often used on cotton, potatoes and soy beans.

(vi) Miscellaneous Herbicides

One such common herbicide used in the U.K. is Glyphosate, discovered in 1971. It is a nonselective, non residual, post-emergence material. It is recognised for its effectiveness against perennial, deep-rooted grass and broad-leaf weeds, as well as woody brush problems in crop and non crop areas. It is a translocated, foliar applied herbicide that can be applied at any stage of plant growth or at any time of year, with most types of application equipment. Its chemical composition is shown below:

GLYPHOSATE (Roundup)



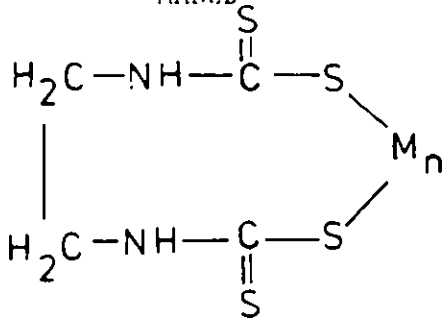
c) Organic Fungicides and Bactericides

The newer organic fungicides possess several outstanding qualities. They are extremely efficient - that is, smaller quantities are required than those used in the past; they usually last longer; and they are safer for crops, animals, and the environment. Most of the newer ones also have very low phytotoxicity and most are readily degraded by soil microorganisms, thus preventing their accumulation in soils.

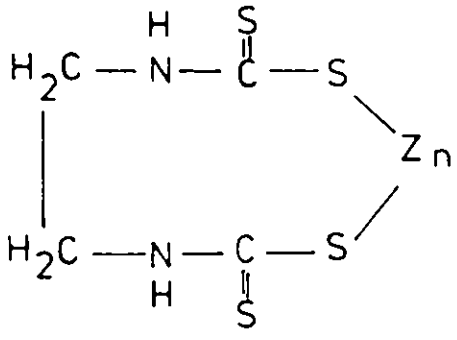
(i) Dithiocarbamates

Among these maneb and zineb shown below, were developed in the early 1940's.

MANEB



ZINEB

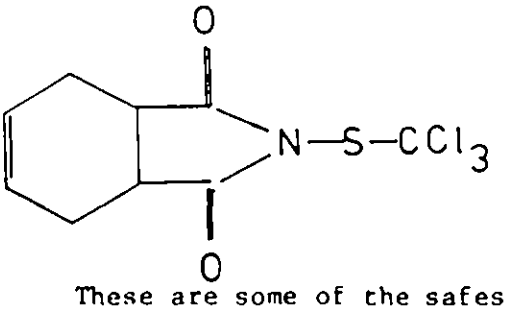


Such fungicides probably have greater popularity and use than all other fungicides combined. Except for systemic action, they are employed collectively in every use known for fungicides.

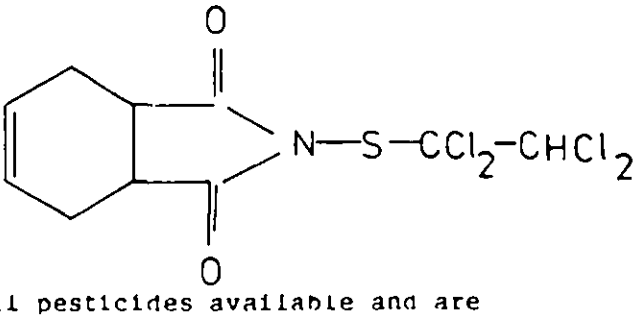
(ii) Dicarboximides

These are foliant protectant fungicides. Captan appeared in 1949 and is undoubtedly the most heavily used fungicide around the home of all classes and captafol appeared in 1961. They are both used primarily as foliage dusts and sprays on fruits, vegetables and ornamentals and are shown below:

CAPTAN



CAPTAFOL (Difolaton)



These are some of the safest of all pesticides available and are recommended for lawn and garden use, as seed treatments, and as protectants for mildews etc.

(iii) Systemic fungicides

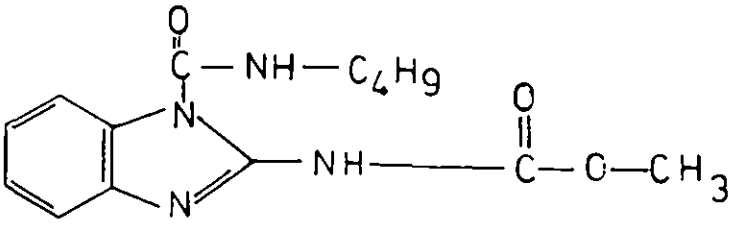
Only in recent years have successful systemic fungicides been marketed. Most have eradicant properties that stop the progress of existing infections. A few can be applied as soil treatments and are slowly absorbed through the roots to give prolonged disease control.

Systemics also reduce the risk of contaminating the environment by fraequent broad fungicidal treatments. Undoubtedly these will gradually replace the protectants that compose the bulk of the fungicides used at present.

(iv) Benzimidazoles

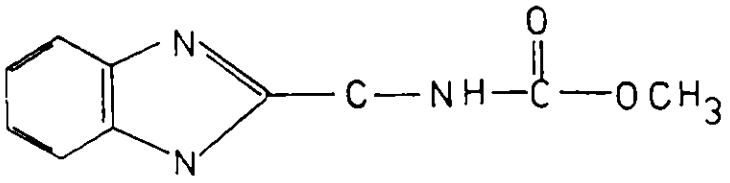
These are commonly represented in the UK by benomyl which was introduced in 1968 and is used against a broad spectrum of diseases. Benomyl (shown below) has the widest spectrum of fungitoxic activity of all the newer systemics.

BENOMYL



Also, carbendazim, introduced in 1973 has proved useful in controlling Dutch elm disease, when injected into tree trunks.

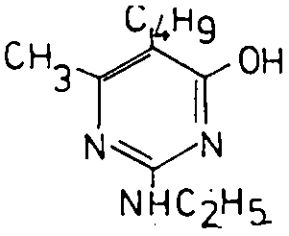
CARBENDAZIM (Lignason)



Pyrimidines

These systemic fungicides appeared in the late 1960s and include ethirimol (shown below):

ETHIRIMOL (Milcurb Super)

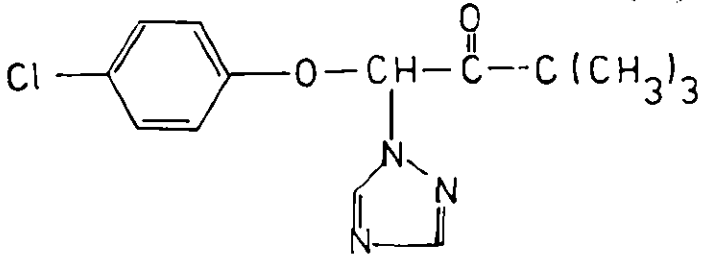


It is very active against specific types of powdery mildews, especially for cereals.

Traizoles

Lastly, Triadimefon is the sole systemic fungicide of the triazole group. It carries both protective and curative actions, and is effective against mildews and rusts on vegetables, cereals, deciduous fruit, grapes and ornamentals.

TRIADIMEFON (Bayleton)



1.4 Pesticide applications techniques

Pesticides are normally marketed as formulated products, ready for use directly or after dilution with water, or some other solvent. The majority of formulations are designed for use as sprays, other types include baits, dusts and granules.

The aim in application is clearly to use a pesticide as economically as possible to achieve the desired result, with minimum harm to the neighbouring environment. However, if a crop is sprayed from the air in

high winds, for example, it will drift and may adversely affect people or livestock, and may destroy plants or hedgerows. Even ground spraying can be so badly done as to cause damage. Various application methods are thus commonly employed in the U.K.

a) Aerial Spraying

There has been an appreciable increase in aerial spraying in recent years (Sly, 1981), as shown below:

Aerial applications (,000 hectares)

Aircraft	1976	1977	1978	1979
Fixed Wing	413	405	339	393
Helicopter	137	177	247	259
Total	550	581	585	653

The above data also includes aerial applications of fertilisers and seed. However, despite this, an indication of the increase is still apparent. The most extensive usage was on cereals, potatoes, peas, beans and oilseed rape. Demeton-S-methyl, triazophos, dimethoate and pirimicarb were the most used insecticides while maneb, fentin acetate/maneb, triadimephon, carbendazim/maneb and tridemorph were the most used fungicides. Application of herbicides and other pesticides from the air accounted for only about four per cent of all applications (Sly, 1981).

It must be remembered that use of the more toxic or persistent chemicals is excluded and any special risks (such as that to bees) is carefully assessed.

Aerial spraying on forests is rarely practised in the UK, but during 1978 the Forestry Commission carried out a large scale operation on forests of lodgepole pine in the North of Scotland, spraying over 5000 hectares with the OP insecticide fenitrothion.

(b) Ultra Low Volume (ULV) and Controlled Droplet Application (CDA)

These techniques are largely associated with herbicides which account for nearly 75 per cent of the active ingredient used in agriculture in the

UK. With these methods, pesticides which are normally applied on farms in fairly diluted form by pumping them through nozzles to form a spray consisting of a mixture of large, medium and small droplets, at typical applications of 250 litres or more of spray mixture per hectare, with so called "low volume" applications ranging upwards of 100 litres/hectare, would be replaced by ULV methods, typically spreading about 25 litres/hectare in a more concentrated form. The associated CDA technique enables this more concentrated form to be projected from a spinning disc in droplets of a more uniform size. Thus, ULV/CDA techniques, if perfected, could lead to a reduction of up to 25 per cent in the total quantity of active ingredient used (DOE, 1979). However, extra precautions are necessary to avoid spray drift of these more concentrated sprays.

1.5 The Risks of Pesticide Use

Two properties of pesticides are particularly relevant to a consideration of their impact on the environment these are their selectivity and persistence.

(a) Selectivity

Many modern pesticides are selective to a greater or lesser extent; that is, they are more toxic to some groups of organisms than to others. The selectivity may be increased by the choice of formulation or by the method and timing of application. However, in recent years due to the high cost of pesticide development, manufacturers have tended to look for chemicals which control a range of pests and diseases.

(b) Persistence

The rate of breakdown of an organic pesticide is dependent on its chemical structure and a wide variety of processes, which are affected by such factors as the soil type and acidity, temperature and moisture conditions. There is a wide range in the times of degradation, as shown in Table 14 below.

Table 14: Relative Persistence of some Major Pesticides Classes

CHEMICAL CLASS	USE	PERSISTENCE
OCs	Insecticides	2-5 years
Ureas	Herbicides	4-10 months
Triazines	Herbicides	3-19 months
Phenoxy	Herbicides	1-15 months
Carbamate	Herbicides, fumigates, insecticides	2-8 weeks
Aliphatic acids	Herbicides	3-10 weeks
OPs	Insecticides	7-84 days

Most of the OC insecticides are highly persisent, ie. they exhibit a very low rate of degradation. The OPs in contrast, persist only for a few days or weeks. It may also be noted however, that with the change to less persistent materials, the active ingredients of insecticides have tended to be more acutely toxic to man and other vetebrates. Although clearly while any such risks are highly localised in their extent, a reduction in spray drifting becomes increasingly important.

Moreover, it is insufficient to consider only the risks to the environment of the chemicals as applied, since some of the metabolic products they give rise to may be more damaging and even more stable than the original compounds, thus causing greater residue problems. For an example, the reader is referred to the work of Pleiva and Gentile (1976) on the herbicide atrazine.

In addition, there remains particular concern about the possible long term effects of the persistent OC compounds such as DDT, aldrin and dieldrin. Because of their early widespread use and their great persistence they have become widely dispersed in the environment and they constitute still the most prevalent and predominant of all pesticide residues in man, entering via the food chain.

1.6 Pesticide Residues in Soil and Water

It is clear that the distribution and fate of pesticides are determined by a host of variables that includes the nature of the pesticide and the many factors that determine the environment in which it is found (McEwen and Stephenson, 1979). Figure 2 depicts some of these factors.

(a) Pesticides in Soil

(i) Sources

Intentional Application

Direct application to the soil surface, incorporation in the top few inches, or application to crops are the routes by which most high concentrations of pesticides reach soil.

Unintentional Application

Large amounts also reach the soil through drift during application and through atmospheric fallout. For example, as much as 50% or more may be lost to the target area during aerial spraying due to variations in wind speed, droplet size and air temperatures. Also, with regard to atmospheric fallout, studies in the 1960's have demonstrated the presence of pesticides in rainwater and/or snow (Table 15).

Table 15 : Pesticides in Rainwater - some highest levels reported

PESTICIDE	AREA	LEVEL (ng/ℓ)	STUDY
DDT	England	^	Wheatley and Hardman (1965)
DDT	England	470	Abbott et al (1965)
DDT	England	46	Tarrant and Tatton (1968)
Dieldrin	England	40	Tarrant and Tatton (1968)
Dieldrin	England	95	Abbot et al (1965)
BHC	England	175	Abbott et al (1965)
BHC	England	260	Tarrant and Tatton (1968)

Source: Adapted from McEwen and Stephenson (1979)

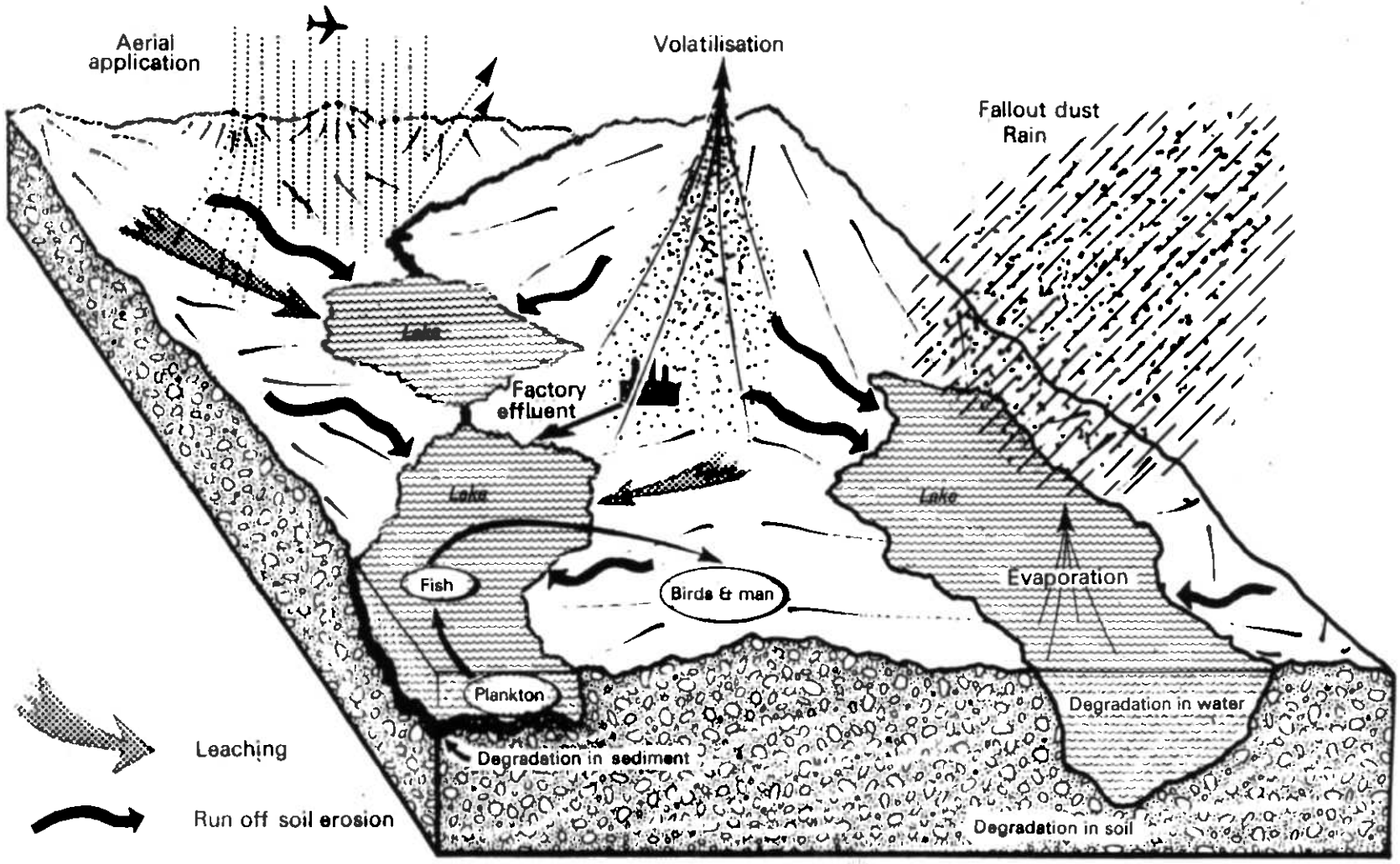


Figure 2. Pesticides in the environment and some factors important in their fate.

Seasonal use patterns generally suggest an explanation for some of the variations observed in the above studies, but not all. However, it is doubtful that the levels present in rainwater are sufficiently high to constitute a major source of soil contamination (Edwards, 1973).

(ii) Fate of Pesticides in Soil

Many factors influence the behaviour and fate of pesticides after contact with soil (Figure 3). These include (1) adsorption to clay and organic matter, (2) leaching with the downward percolation of water, (3) volatilisation to the atmosphere, (4) uptake by soil organisms or plants, movement with runoff water or eroded soil, (6) microbial degration, (7) chemical degradation, and (8) photolysis of primary importance is the chemical nature of the pesticide and the soil type. Environmentally the processes of adsorption and desorption are crucial since they influence most of the other processes determining the eventual fate of a pesticide.

Adsorption

Pesticides have varying tendencies to be adsorbed or attracted to clay or organic matter particles or to be dissolved in the soil solution. For the most part the adsorption sites on clay or organic matter are negatively charged and constitute the "Cation Exchange Capacity" of a particular soil. For each pesticide, soil type, and set of soil conditions, a different equilibrium is established between the amount adsorbed and the amount dissolved in the soil solution.

Soil Type

Of special importance are the soils clay and organic matter content, for these are colloidal and have a high cation exchange capacity and surface area. Thus, higher rates of pesticide application are required for effective control if soils are high in either clay or organic matter, since in such soils, much of the pesticide is adsorbed and not active, therefore producing more persistent residues.

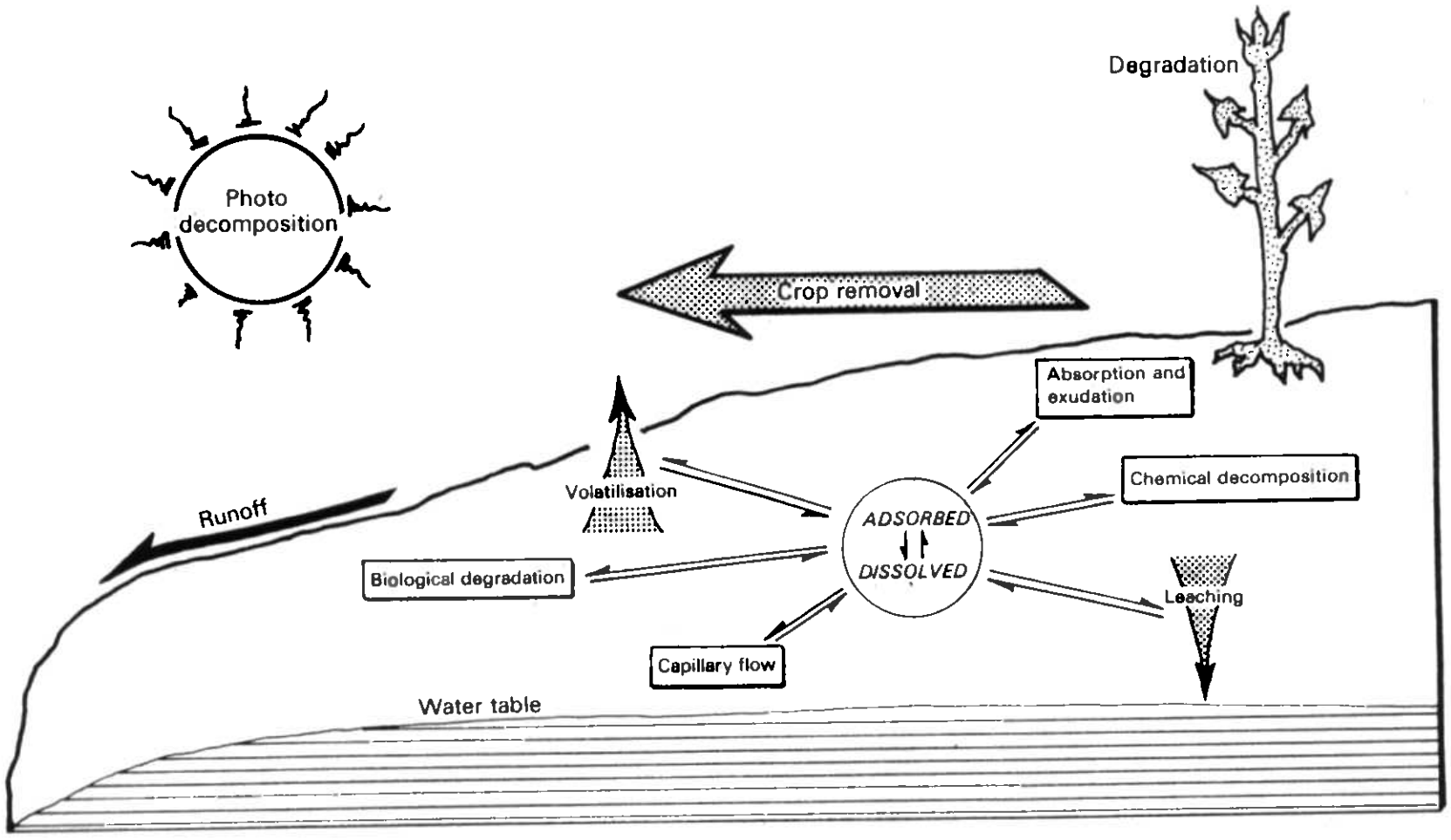


Figure 3. Processes influencing the behaviour and fate of pesticides in the soil environment (redrawn and modified from Weber et al., 1973).

Nature of the Pesticide

The chemical structure of a pesticide determines sorption equilibrium by influencing its direct affinity for the clay or organic matter, or by influencing its solubility or affinity for the soil solution. Many investigators have noted a general but not precise inverse correlation between pesticide solubility and adsorption (McEwen and Stephenson, 1979). Also, granular formulations are usually the most persistent. Wettable powder and dust are often less persistent than emulsifiable preparations.

Soil Moisture Content

One would expect more pesticide to be adsorbed in dry soils. This is true in moderately light to very light soils, but not in heavy soils, however (McEwen and Stephenson, 1979). Thus, because water molecules are themselves polar they begin to compete with the pesticide molecules for adsorption sites on the soil colloids, forcing more of the pesticide into solution.

Soil pH

The fate of pesticides in soil varies with pH, primarily because of the influence of pH on sorption. Soil pH also affects chemical degradation and thus pesticide adsorption is usually highest in more acid soils. However, within normal pH ranges, slight increases in acidity may convert pesticides from negatively charged anions to uncharged molecules or even to positively charged cations, and thus dramatically increase their sorption. But, when soils are extremly acid, most of the cation exchange sites are occupied by hydrogen cations, and pesticide adsorption is consequently low due to the lack of negative sites. Adsorption is also very low at extremely high pHs.

Soil Temperature

Pesticide adsorption in soil is an exothermic process. When hydrogen or ionic bonds are formed, heat is given off. Thus, when the soil temperature increases, the input of heat can break some of these bonds and cause desorption of some pesticide molecules.

Leaching

Solubility is an important aspect related to pesticide persistence in soil. Within limits, pesticides highly or moderately soluble in water are leached from soils more quickly than those that are less soluble.

Movement with Runoff water

As water moves laterally over a sloping soil surface, pesticides can be described and moved with runoff. Lateral movement is likely to be greatest under conditions of least adsorption.

Movement with Eroded Soil

No soil applied pesticide is immune to transport if it is adsorbed onto soil particles. The longer it remains adsorbed at or near the soil surface without degration, the more likely it is to be eroded.

Volatilization

Several factors influence pesticide volatilization. The structure of the chemical is important since it determines its vapour pressure. Cool, dry conditions in soils with high organic matter or clay content, normally result in very little loss of even the most volatile chemicals, since they are adsorbed tightly. Conversely, warm, moist conditions give greater desorption and greater volatilization losses.

Microbial Degradation

The primary microorganisms in soil are algae, fungi, actinomycetes, and bacteria. Most of these are dependent on organic compounds for energy and growth. When an organic pesticide is added to soil and reaches an equilibrium between the soil colloids and the soil solution, any molecules in the soil solution are immediately attacked as potential energy sources.

Thus, any factors that encourage the growth of degrading microorganisms or that increase the availability of the pesticide in the

soil solution will enhance the disappearance of the chemical. Thus, conditions such as warm temperatures, adequate soil moisture and aeration, unextreme pH, and adequate fertility, encourage microorganisms and increase desorption and the availability of pesticides.

Chemical degradation

Chemical reactions in soil can destroy the activity of some pesticides and activate others. Whereas adsorption normally decreases microbial degradation rates, it may enhance the chemical degradation of some compounds. In chemical degradation pH is important, but its exact influence varies for different pesticides. For example, the herbicide atrazine degrades faster at a low pH (Armstrong and Chesters, 1968), whereas malathion breaks down quicker at a high pH.

Photodegradation

Few organic pesticides are completely resistant to photolysis, but it is probably not a major means of pesticide inactiviation or disappearance in soil.

(iii) Conclusion

It is clear that there are many different processes that influence the movement, persistence and activity of pesticides in the soil. It is also clear that there are countless ways in which these processes can interact, as seen in Figure 4.

However, with few exceptions, the only pesticide residues reported in soil surveys have been either persistent inorganic chemicals such as arsenic, that were used as insecticides prior to 1945, or persistent O.C. insecticides (Edwards, 1973). Residues of very few OP insecticides have been reported from areas of intensive use. Unfortunately, little information exists for UK soils (Edwards, 1973).

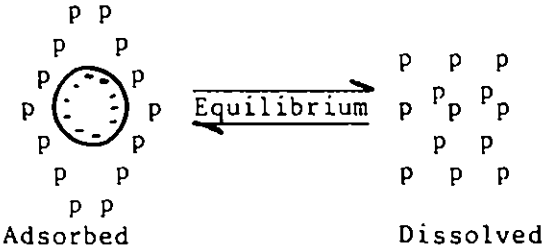
In almost all the UK soils surveyed the commonest chemical has been DDT, with the next most common being dieldrin. Few others have been found in UK soils as seen in Tables 16 and 17.

Factors resulting in
greater desorption

1 Higher soil temperature.
2 Higher pesticide solubility within related groups.
3 Higher soil moisture content in light soils.
4 Greater percent sand.
5 Higher soil pH.

Adsorbed pesticides
are more likely to:

1 Move with eroded soil.
2 Be taken up by earthworms if lipophilic.
3 Be degraded chemically.



Desorbed pesticides
are more likely to:

1 Volatilize from the soil.
2 Move downwards by leaching.
3 Move laterally with run-off water.
4 Be degraded by microorganisms.
5 Be taken up by higher plants.

Factors resulting in
greater adsorption:

1 Higher clay content.
2 Higher organic matter content.
3 Greater polarity of the pesticide molecule.
4 Cationic nature of the pesticide molecule.

Figure 4 Interrelationship of processes influencing the fate of pesticides in soil.

Table 16 **Residues of DDT and related compounds in soil**

Location	Reference	No. Sites	Crop	Residues in ppm Max	Mean
Orchards & Vineyards					
G.B.	Edwards, 1969		Fruit	131.1	61.8
Agricultural					
G.B.	Wheatley et al, 1962		Potatoes	0.96	0.2
G.B.	Davis, 1968		Mixed	0.80	0.3

Source: Edwards (1973)

Table 17 Residues of other organochlorine insecticides in soil

Location	Reference	No. Sites	Crop	Residues in ppm Max	Mean	
Horticultural						
G.B.	Edwards, 1969		Carrots	1.47	0.68	(Dieldrin)
Agricultural						
G.B.	Wheatley et al, 1962		Potatoes	0.12	0.12	(Aldrin)
G.B.	Davis, 1968	10	Mixed	0.7	0.15	(Aldrin)
				0.7	0.15	(Dieldrin)
G.B.	Edwards, 1969		Cereal	0.5	N.A.	(Y-BHC)

Source: Edwards (1973)

(b) Pesticides in water

The widespread use of pesticides makes it inevitable that a portion of these will contaminate surface waters (McEwen and Stephenson, 1979). Hence, water, and the mud at the bottom of rivers are major reservoirs for persistent residues.

(i) Sources

Waters are contaminated in the same way as soils through pesticide drift during application and as atmospheric fallout of rain and dust. Additionally, water may be contaminated through soil erosion, industrial effluent, sewage and occasionally by spills into, or adjacent to, water courses.

Atmospheric fallout

It is established that rain water contains pesticides. Some contamination also occurs by the settling of atmospheric dust. No precise data, however, exists.

Soil Erosion

Where pesticides are applied to land, those soluble in water may be carried to nearby waters by surface runoff, and either soluble or insoluble pesticides may be carried on soil particles in runoff or eroded by wind.

Industrial effluent

Many industries use pesticides in the manufacture of their products, and effluents may contain high levels. Many instances have been reported where DDT, lindane or dieldrin has been discharged from carpet or fabric manufacturing plants, where they are used for mothproofing.

Sewage

Pesticide sources in sewage include some discharges from industry, residues from homeowner's use, and a variety of fungicides and bactericides

used in soaps and cosmetics. The level of contamination may be high. Edwards, (1973) cites instances where dilutions of 1:20 were required before effluents would be safe for fish. For some pesticides, for example, hexachlorophene, urban wastewaters probably represent the major source (Sims and Pfaender, 1975).

Spills

The handling of pesticides in the volumes now used increases the possibility of large-scale industrial spills during processing, storage and transportation, as well as the problem of smaller spills by individual applicators.

(ii) Fate of pesticides in water

The persistence of pesticides in water depends on a number of factors, only some of which can be qualified and/or quantified. Those that persist in soil also persist in water or in river sediments, from which mixing with the overlying water constantly occurs.

Nature of the pesticide

With organic pesticides those that are highly soluble are hydrolyzed rapidly and have a short life in water. Among the pesticides, DDT, dieldrin and endrin are the most persistent, as each are relatively insoluble in water (0.2 ppb, 186 ppb and 100 ppb, respectively) and resistant to hydrolysis. Hence, these have the potential to persist in rivers and river sediments. For most pesticides however, persistence in water is brief, irrespective of their solubility.

Nature of the Water

The natural composition of the water also plays an important role in the fate of pesticides in water.

Chemical composition

Some studies have considered water hardness (as $CaCO_3$) as important. However while some indicate that hardness is important in determining toxic effects, others indicate that it has little effect on persistence and toxicity (McEwen and Stephenson, 1979).

pH

Since many pesticides degrade by hydrolysis it might be assumed that water pH would be important. However, although laboratory findings make it clear that pH is important to degradation it may be of only minor significance in natural waters (McEwen and Stephenson, 1979).

Temperature

Increases in temperature increase the rate of chemical reaction and the rate of volatilization of pesticides. Within limits they will also increase biological activity and thus would be expected to increase biological degradation of pesticides.

Aquatic Life

Numerous studies attest to the fact that a wide range of plants and animals detoxify pesticides. Any consideration of the biota to which pesticides are exposed, must include that of the bottom mud, where anaerobic and near anaerobic conditions prevail. Some of the mechanisms involved in bilogical degradation include oxidations, dechlorinations, reductions, hydrolyses, and ring cleavage.

Of all the groups involved, microorganisms are probably most important.

Sediment and Suspended Matter

Many studies indicate that bottom sediments in rivers act as

reservoirs for persistent pesticides. Analysis of suspended matter demonstrates a tendency for pesticides to become adsorbed or absorbed to particulate matter whether organic or inorganic, living or dead.

(iii) Residue levels in surface waters

Estimates have been made of the "safe" level for pesticides in drinking water and Ettinger and Mount (1967) have noted the potential for fish to accumulate some pesticides, suggesting maximum levels in water which would give a reasonable measure of fish safety (Table 18). More recently, maximum permissible levels have been recommended to protect fish and aquatic life (Committee, 1973). These are much lower (see Table 18).

Also, a number of studies have correlated pesticide levels in streams with local use patterns and rainfall. Thus, Miles and Harris (1971) found that the highest levels of DDT in streams in an agricultural area reflected spring runoff and rainfall patterns throughout the growing season. Thus, sheet erosion probably constitutes a major source of contamination.

Many of the factors that determine persistence in soils apply to the problem in water. Table 19 gives a summary of the relative persistence of some pesticides in natural waters (McEwen and Stephenson, 1979).

In British rivers, only DDT, BHC, aldrin and dieldrin had been reported up to 1973. Up to then, only two surveys were available. The first was a study in 8 south east rivers and 18 rivers from other parts of the country (Croll, 1969). The amounts reported were relatively small, being generally less than 50 ng/ℓ, the occasional larges residues were attributed to industrial effluents (Table 20). There were no residues in the 12 different groundwater samples analysed.

TABLE 18 Levels of some pesticides permissible in potable water and safe levels for surface waters[a]

Pesticide	Permissible Level[ab]	Maxmimum Suggested	
		Fish[ac]	Aquatic Life[ab]
Dieldrin	1	0.25	0.005
Endrin	0.5	0.1	0.002
DDT	50	0.5	0.002
Heptachlor	0.1	1.0	0.01
Aldrin	1	0.25	0.01
Lindane	50	5.0	0.02
Chlordane	3	0.25	0.04
Methoxychlor	1000	20.0	0.005
Toxaphene	5	2.5	0.01
2,4-D	20	not given	--
2,4,5-TP(Silvex)	30	not given	--
2,4,5-T	2	not given	--
Organophosphorous plus carbamates	100	not given	

[a]Level expressed as parts per billion.

[b]From Committee, 1973.

[c]From Ettinger and Mount, 1967

TABLE 19 Relative persistence of some pesticides in natural waters

Non Persistent[a]	Slightly Persistent[b]	Moderately Persistent[c]	Persistent[d]
azinphsmethyl	aldrin	aldicarb	benomyl
captan	amitrole	atrazine	dieldrin
carbaryl	CDAA	ametryne	endrin
chlorphyrifos	CDEC	bromacil	hexachlorobenzene
demeton	chloramben	carbofuran	heptachlor
dichlorvos	chlorpropham	carboxin	isodrin
dicrotophos	CIPC	chlordane	monocrotophos
diquat	dalapon	chlorfenvinphos	
DNOC	diazinon	chloroxuron	
endosulfan	dicamba	dichlorbenil	
endothal	disulfoton	dimenthoate	
fenitrothion	DNBP	diphenamid	
IPC	EPTC	diuron	
malathion	fenuron	ethion	
methiocarb	MCPA	fensulfothion	
methoprene	methoxychlor	fonofos	
methyl parathion	monuron	lindane	
mevinphos	phorate	linuron	
parathion	propham	prometone	
naled	Swep	propazine	
phosphamidon	TCA	quintozene	
propoxur	thionazin	simazine	
pyrethrum	vernolate	TBA	
rotenone		terbacil	
temephos		toxaphene	
TFM		trifluralin	
2,4-D			

[a] Half-life less than 2 weeks

[b] Half-life 2 weeks to 6 weeks

[c] Half-life 6 weeks to 6 months.

[d] Half-life more than 6 months

Source: McEwen and Stephenson (1979)

TABLE 20 *Residues of organochlorine insectitudes in water*

Location	Ref	No Sites	BHC		Dieldrin		DDT R	
			Max	Min	Max	Min	Max	Min
GB	Croll, 1969	76 British rivers (2 monthly samples)	118.0	25.82	423	25.16		
GB	Croll 1969							
GB	Croll, 1969	15 British rivers (single samples)	214	53.64#	2840.0	291.64#	43+	8.67
GB	Lowden et al, 1969	9 British rivers	98	18.7	40	3.3	15	1.6
GB	Lowden et al, 1969	9 Yorkshire rivers	180	38.6	630	114	908	64.6
GB	Lowden et al, 1969	21 Sewage effluents	390	92.5	1900	145	800	130.9
GB	Lowden et al, 1966	Sewage effluents			300	200	130	36

+ residue found at only one site

affected by a few large values

Source : Edwards (1973)

(c) Drinking Water Quality and Pesticides

The WHO guidelines for drinking water quality with regard to organic constituents are presented in Table 21. Many of these organic constituents are potentially toxic and can reach surface or groundwater either from point or non-point sources. Many too are carcinogenic and a number have been shown to be mutagenic.

In some cases where no threshold of toxicity exists, such as carbon tetrachloride multistage extrapolation models have been used to give an indication only, of potentially harmful levels to individuals and communities.

No reasonable person would dispute the immense usefulness, in terms of food production and health protection, of the wide range of pesticides now available to mankind. Equally, it would be absurd to suggest that these chemicals should be utilised without any controls designed to protect human beings and the ecosystem from harmful effects resulting from this use.

In water, the CEC Directive sets two maximum allowable concentrations for pesticides and related products, including insecticides, herbicides, fungicides, PCB and PCT (Table 22). These are:

a) for substances considered separately 100 ng/l
b) for all such substances, 500 ng/l

A comparison shows that, for the small number of pesticides and related compounds covered in the WHO guidelines the total concentration is 134 µg/l compared to only 0.5 µg/l (i.e. 500 ng/l) for all pesticides and related products allowed by the CEC Directive. Hence, one figure is 268 times the other. Clearly there is a danger that unenforceable or ill-considered controls could lead to disregard of the whole problem of pesticides in drinking water as will be seen later.

d) Some recent case studies of pesticide residues in river waters

(i) Pesticide Pollution in Australia

Garman and Sutherland (1983) have studied the extent of pesticides as non-point source pollutants in Australia. As in the U.K., herbicides

TABLE 21 WHO Guidelines for drinking water quality

Organic Constituents	
Substance	Guideline value (µg/l)
Aldrin and Dieldrin	0.03
Benzene	10
Benzo-a-pyrene	0.01
Carbon tetrachloride	3
Chlordane	0.3
Chlorobenzene	no guideline set
Chloroform	30
Chlorophenols	no guideline set
2:4D	100
DDT	1
1:2-Dichloroethane	10
1:1-Dichloroethane	0.3
Heptachlor and Heptachlor epoxide	0.1
Hexachlorobenzene	0.01
Gamma-HCH (Lindane)	3
Methoxychlor	30
Pentachlorophenol	10
Tetrachloroethane	10
Trichloroethene	30
2:4:6-Trichlorophenol	10
Trihalomethanes	no guidelines set

TABLE 22A EEC directige for drinking water quality A1.1 pesticides and related products (including PCBs)

	Directive level (µg/1)
For any one substance	0.1
For all substance together	0.5

22B WHO Guidelines for drinking water quality pesticides (only 8 categories covered)

	Guideline value (µg/1)
DDT	
Aldrin and Dieldrin	0.03
Chlordane	0.3
Hexaclorodbenzene	0.01
Heptachlor and Heptachlor Expoxide	0.01
Gamma HCH (Lindane)	3
Methoxyclor	30
2:4D	100
TOTAL	≈ 134

i.e. Total concentration suggested by WHO guidelines (for only 8 pesticides) is 268 times allowable concentration for all pesticides under EEC directive

account for a large proportion (about half) of total sales, and OC pesticides use has given way to increasing use of OPs and Pyrethroids. The main mechanisms of transport were spray drift (as much as 75% loss from target areas depending on climatic conditions) and surface runoff. The types and amounts of pesticides transported in runoff depended on:

(1) Frequency and rates of application
(2) Application methods e.g. foliar, soil incorporation.
(3) The persistence, volatility and mobility of the compounds
(4) The intensity and duration of runoff events
(5) Elapsed time between applications and storm events.

The amounts of surface runoff inputs in agricultural lands were assessed for a range of catchments and agricultural land uses (Garman and Sutherland, 1983). Total exports of DDT, Dieldrin and Linuran ranged from 0.004% to 0.006%, 0.035 % to 0.31% and 0.02% to 0.03% respectively. The results of this AWRC study were thus consistent with, although generally much lower than, the working limits for losses suggested by Wauchope (1978) on the basis of U.S. studies:

(i) Average losses of 1% for foliage applied OC insecticides
(ii) Losses of 2% - 5% for wettable powder-formulated herbicides (e.g. atrazine and Limuran).
(iii) Losses of 0.5% for non OC insecticides, incorporated insecticides and all other herbicides.

Of course significantly higher losses may occur in particular circumstances such as an intensive storm immediately after treatment.

The effects of pesticide runoff on receiving waters were also investigated. Maximum concentrations of DDT were lower than the recommended drinking water limit (1 µg/l), except for storm runoff and drainage flows from some intensive agricultural areas. However DDT concentrations did exceed the criterion for the protection of aquatic life (0.001 µg/l) in about 10% of samples, by up to 3 times. Maximum concentration of dieldrin tended to be higher than for DDT, but below their drinking water limit (1 µg/l) except in storm flows from cultivated lands. Dieldrin was also detected in a significant percentage of samples (up to

50%). Mean concentrations exceeded the criterion for protection of aquatic life by up to 2 times.

(ii) Pesticide pollution in runoff in the U.S. and Canada

Weber, Shea and Strek (1980) have evaluated nonpoint sources of pesticide pollution in runoff in the U.S. Firstly, they evaluated the pesticide runoff found during seasonal or long-term studies. Generally, the loss of pesticides in runoff was found to be relatively low, averaging 2.39% for atrazine, 0.54% for Cyanazine, 1.33% for Simazine, 0.33% for 2,4-D, 1.08% for Carbofuran, 0.12% for Linuran, 0.36% for Toxaphene and 0.22% for Trifluralin, for example. The highest amount of runoff from any one pesticide was 15.9% of the total applied for atrazine. The next highest losses were 7.2, 6.1, 5.7, 5.7, 5.4, 5.4 and 5.1 percentages for diphenamid, propazine, terbuthylazine, atrazine, atrazine, simazine, and atrazine, respectively. Hence, the highest losses were from the wettable powder formulations, especially when they are applied to the soil surface. Higher losses also occurred from bare soil cover.

Secondly, maximum concentrations found during short-term runoff studies were evaluated. The maximum pesticide concentrations found in runoff sediment were 40, 30, 21.8, 13, 12, and 11 ppm for arsenic acid, terbuthylazine, propazine, fluometuron, dieldrin and atrazine, respectively. The highest concentrations found in the solution and sediment phase were 5.2, 4.8, 4.7, 4.2, and 4.2 ppm for picloram, dicamba, atrazine, 2,4-D salt, and picloram, respectively.

Numerous case studies of pesticide losses in individual catchments in North America also exist. For example, Nicholaichuk and Grover (1983) looked at the losses of 2,4-D applied to wheat in South Western Saskatchewan. The loss was greater from the treated stubble compared with fallow, which served as a control. Average losses were 4.1% of the amount applied and correlation analysis showed the amount of loss to be a function of runoff. Hence, a simple correlation of runoff volume and losses from an application rate of 0.42 kg/ha for the 6-year period resulted in the following equation:

$$Y = 0.45\ X - 2.3 \quad (r^2 = 0.96)$$

where Y = herbicide loss (g/ha), and X = runoff volume (mm). However, the

average flow-weighted mean concentration of 31 µg/l was well below the USEPA maximum permissible level of 100 µg/l.

Finally, in the U.S., Wu, Correl and Remenapp (1983) have recently investigated herbicide losses in runoff from experimental watersheds in the Rhode River region of Maryland. Both atrazine and alachlor (herbices used in cornfields) were investigated. Although alachlor was applied in greater quantities, atrazine was detected more frequently in runoff waters and at greater concentrations than alachlor (0.40 µg/l vs 0.6 µg/l). Atrazine was also more persistent and more mobile in watershed soils. Lastly, a major portion of atrazine was found in dissolved aqueous form in runoff samples collected during storms, with percolation in subsurface flow and dissolution in overland flow believed to be the important transport mechanisms.

1.7 A U.K. Water Authority Perspective

Initial indications of the respective water authorities perspective of any pesticide pollution problem in the UK have been assessed based on their response to a letter sent from the authors. To date, the Welsh Water Authority has indicated the existence of localised problems in connection with sheep dipping and aerial spraying of bracken, (Buckley, pers comm 1985). Severn Trent W.A. have also indicated the existence of some problems, especially in connection with herbicide usage. However, most detailed responses have arisen from meetings arranged with Thames, Yorkshire and Anglian water authorities.

(a) Thames W.A.

The major problem seems apparent rather than real and has been created by the blanket application of the EEC guidelines on drinking water, which calls for a maximum permissible concentration of 500 ng/l for <u>total</u> pesticides and 100 µg/l for <u>individual</u> pesticides, after treatment. In the case of the Thames W.A., concentrations of the herbicides simazine and atrazine in the river water used for supply, exceed the individual limits. The authority favours a change in the application of the limits, rather than treatment of its waters for compliance. In addition, the <u>actual</u> source of these two herbicides is unknown, although it is likely to be agricultural. However, other pesticide sources in the area include power station cooling waters treated with algacides and bactericides and paper

mill discharges. Some concern about more localised pollution was also expressed in connection with the aerial spraying of oil-seed rape and potatoes, in particular.

(b) Yorkshire W.A.

In Yorkshire, the major concern lies with pesticide residues in non-water supply rivers (Edwards, pers comm 1985). In particular, the discharge of textile industry effluents into sewage works. Such industry commonly uses dieldrin, lindane and some pyrethroids for moth proofing. Of most concern are the levels of lindane (HCH containing 99 percent gamma isomer, an OC insecticide) which often exceed the EEC limit in affected rivers by two or three times. Lindane is used mostly by the wool textile industry to treat incoming fleeces.

Apart from the problems experienced in the industrialised south of the Y.W.A. area, some pesticide pollution of a localised nature is also in evidnce in the rural north, which provides most of the water supply. However, most of these problems involve spillages, for example, of diquat into the River Calder.

(c) Anglian W.A.

To date, Anglian W.A, has produced the most informative assessment of herbicide pollution at least (Croll, 1984). In 1982, the authority initiated a survey of all its water resources and included in it, analysis for a number of common herbicides, notably MCPA, Mecoprop, MCPB, 2,4-D, atrazine and simazine. Up to September 1984 concentrations of Mecroprop were found ranging from 0.2 to 2.7 µg/l in surface waters and 0.2 to 0.4 µg/l in groundwaters. MCPA was detected less frequently than mecoprop in surface waters (0.2 to 2.3 µg/l) only. Also, 2,4-D was detected less frequently than either of the above in surface waters at levels of 0.2 to 2.5 µg/l and in underground waters at 0.2 to 2.5 µg/l. Meanwhile, atrazine was found in almost all surface waters at concentrations of 0.2 to 1.4 µg/l, but less frequently in groundwaters (0.2 to 0.5 µg/l). Croll (1984) concluded that it was more likely that its presence at most points arose from total weed control on railway embankments, roadsides and industrial areas, rather than an agricultural use. Lastly, while simazine was detected at most sites where atrazine was found. Levels were generally only 25% of those of atrazine. Although the concentrations detected are

not suspected to cause problems of toxicity, taste etc. in potable waters, they do however, exceed the EEC "Drinking Water" Directive limits for pesticides.

1.8 Modelling Pesticides in the aquatic environment

Numerous investigators in the U.S. have developed models for assessing water pollution from nonpoint sources as indicated by Haith (1982). Bailey et al (1974) and Leonard et al (1979) have developed models which quantitatively describe pesticide runoff as a function of pesticide and soil properties, agricultural practices, watershed characteristics, and climatic factors. Unfortunately, as indicated by Dickinson and Wall (1977), many such models suffer from the following weaknesses: a) the components and parameters are of a conceptual rather than physical nature b) an inadequate characterization of the dynamic development of basin drainage systems c) no identification of the soil moisture storage concepts d) no description of micro-drainage systems, and e) insufficient emphasis on the role of large storms. In addition to these deficiences, most models: a) assume instantaneous equilibrium between adsorbed pesticides and those in solutions, b) assume completely reversible adsorption processes for all pesticides, c) apply uniform equations to all organic chemicals regardless of their chemical properties, d) assume that the diffusion and hydrodynamic dispersion of organic chemicals are insignificant, even for volatile chemicals, e) assume saturated flow conditions, and f) they do not include chemical decomposition and volatilization losses.

However, notwithstanding the above limitations, a brief review of some of the available pesticide models is presented in an effort to indicate the possibility of their successful development in the British context.

a) Agricultural Runoff Management (ARM) model (Donigan et al, 1977)

Skogerboe (1982) described the above model as a continuous one which simulates rainfall, sediment, pesticides and nutrient contributions to stream channels from both surface and subsurface sources. In this model, pesticide adsorption/desorption and degradation are modelled. In order to simulate vertical movement and transformations of pesticides and nutrients in the soil profile, specific soil zones (and depths) are established so that the total soil mass in each zone can be computed. Total soil mass is a necessary ingredient in the pesticide adsorption/desorption reactions and

nutrient transformations. The vertical soil zones simulated in the ARM model include the surface, upper, lower and groundwater zones. The depths of the surface and upper soil zones are specified by the model input parameters, and are generally 2 - 8 mm and 75 - 150 mm, respectively. The upper zone depth corresponds to the depth of the incorporation of soil-incorporated chemicals.

The transport and vertical movement of pesticides and nutrients, as conceived in the ARM model, is indicated in Figure 5. Pollutant contributions to the stream can occur from the surface zone, the upper zone, and the groundwater zone. Surface runoff is the major transport mechanism carrying dissolved chemicals, pesticide particles, sediment, and adsorbed chemicals. The interflow component of runoff can transport dissolved pesticides or nutrients occurring in the upper zone. Vertical chemical movement is the result of infiltrating and percolating water. From all the zones, uptake and transformation of nutrients and degradation of pesticides is allowed. The groundwater zone is however, considered a sink for deep percolating chemicals.

b) Chemicals, Runoff and Erosion from Agricultural Management Systems: the CREAMS model.

Knisel (1982) has reported on the CREAMS model which also considers the effects of agricultural non-point source pollution and includes a consideration of pesticide modelling. The model was designed for field-size areas and was physically based, not requiring calibration. Also, input data requirements were restricted to readily available or easily measurable information. Thus, the adopted system for the evaluation of non-point source pollution in CREAMS, is shown in Figure 6. CREAMS is a state of the art field-scale model for evaluating response from alternative agricultural management practices. Also, the model can be used to develop resource conservation practices, however, it is not a predictive model in absolute quantities, but it provides estimates of the relative response among different management practices.

It has three major components (programs): hydrology, erosion, and chemistry. Each operates separately, and generates information to be used with the next component.

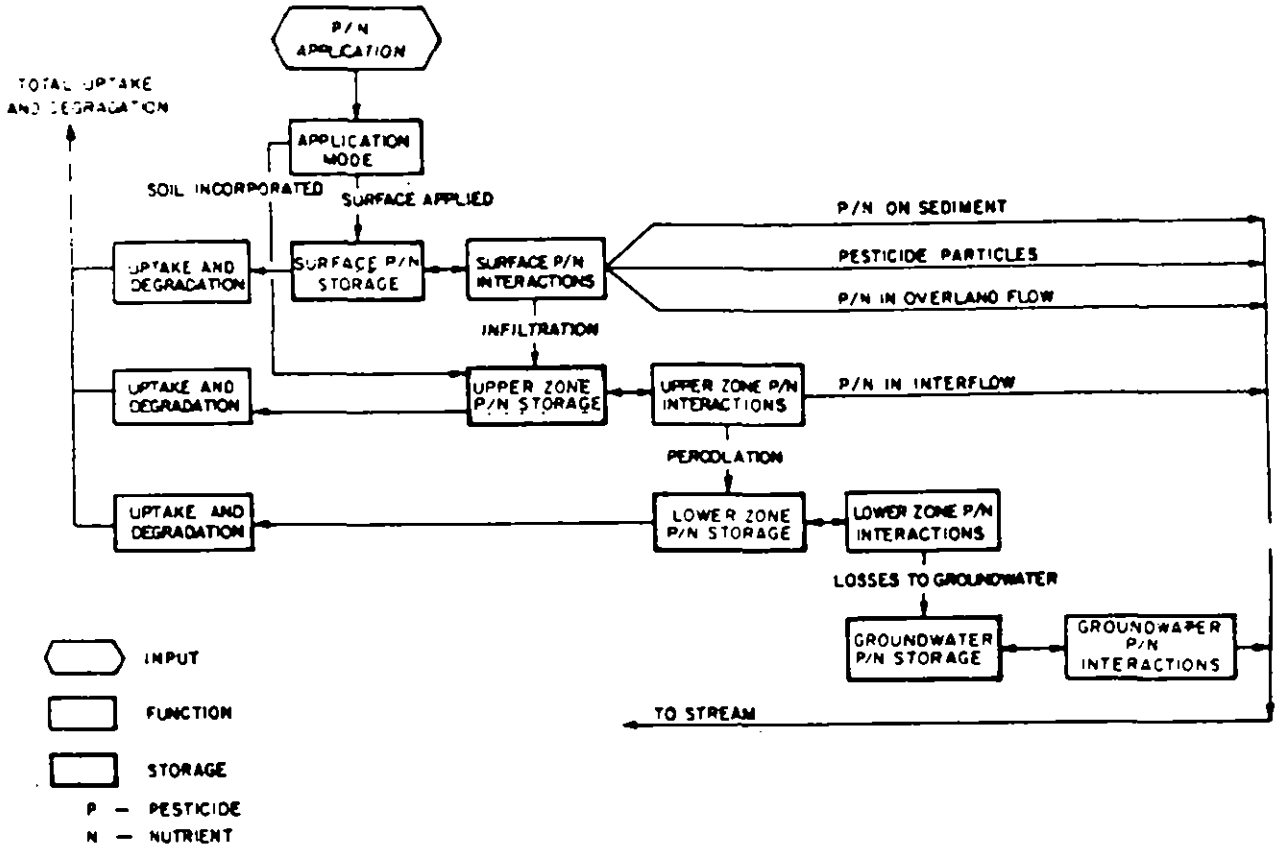


FIGURE 5 Pesticide and nutrient movement in the ARM model

Source: Skogerboe (1982)

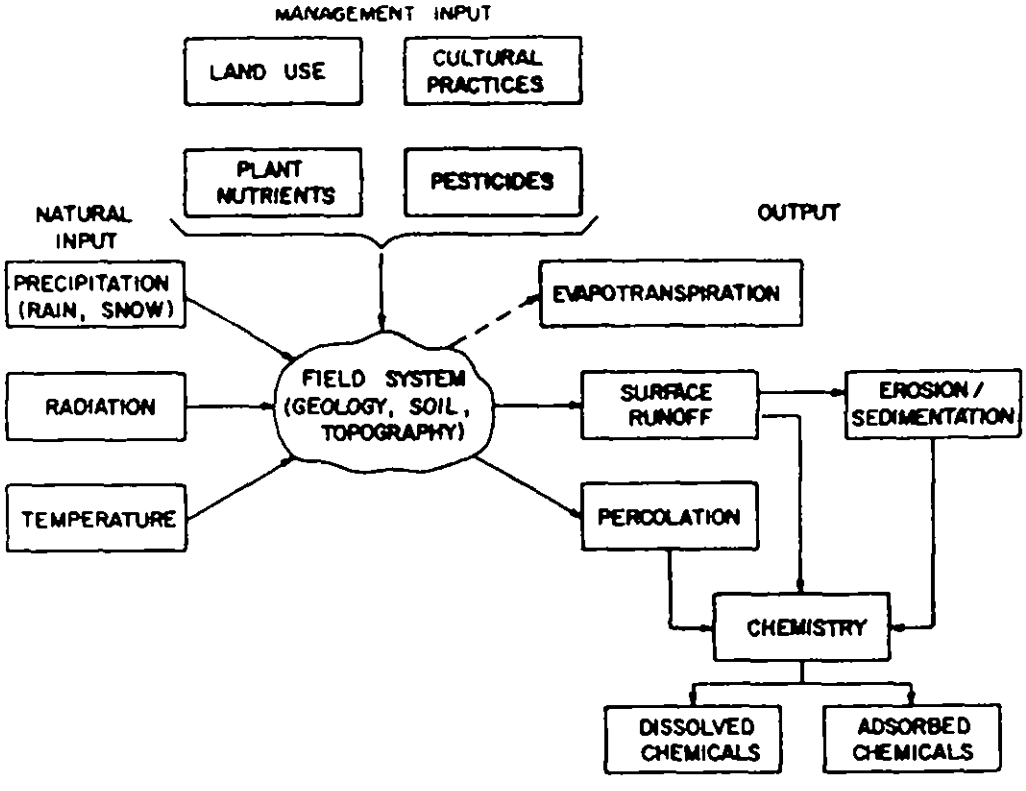


FIGURE 6 System for evaluation nonpoint-source pollution.

Source: Kuisel (1982)

The hydrology component estimates the water balance elements with options for calculating direct runoff. One option requires daily rainfall, the other, hourly or intensity data and uses an infiltration equation to partition rainfall into infiltration and direct runoff. The hydrology component calculates storm runoff volume and peak rate, storm rainfall energy, percolation, and soil water accretions for each storm event. Between storm events, evaporation, transpiration, percolation, and soil water content are calculated.

The erosion component calculates rill and interrill erosion, transport and deposition for any shape of overland flow profile. Sediment transport from overland flow is inputted to the concentrated-flow area or channel. Sediment yield at the field edge and sediment enrichment ratios, based on particle-size distribution, are calculated for use in the chemistry component.

The chemistry component considers both plant nutrients and pesticides. It calculates water and sediment fractions of pesticide load for the field. Foliar applied, soil-surface applied, and soil incorporated pesticides are considered. Multiple applications can also be simulated.

Nutter et al (1984) have simulated herbicide concentrations in stormflow from small forested watersheds using the CREAMS breakpoint hydrology and pesticide options. CREAMS accurately predicted hexazinone concentrations (a triazine herbicide) in the initial stormflow, but underestimated concentrations in stormflow two months or more after the application. In addition, the daily rainfall option of CREAMS was used to evaluate the relative risk of bromacil, picloram, dicamba, and triclopyr, as well as hexazinone, appearing in stormflow, following their application. The model predicted the following order of potential residue appearance in stormflow: bromacil triclopyr hexazinone picloram dicamba. In general, hexazinone losses averaged 0.53 percent of that applied. The underestimates for hexazinone after the first 75 days may have been due to a change in the source of the pesticide during stormflow (Nutter et al, 1984). Clearly the current version of CREAMS which does not account for subsurface movement, tends to underpredict concentrations which may be influenced by subsurface interflow.

c) A Simple Pesticide Runoff Model (Haith, 1980)

Although runoff is not the only pesticide transport mechanism, it may in many situations be the most significant pathway for entry to aquatic systems. Data from field studies provide a valuable means of estimating losses in runoff. However, these losses are influenced by many factors in endless combinations. Hence, the principal methods available for site and pesticide specific analyses of pesticide runoff are likely to be mathematical models.

There appears to be a need for a relatively simple pesticide runoff model which can be used to evaluate lossses for a wide range of field conditions and pesticide characteristics (Haith, 1980). The model proposed is based on commonly used methods of runoff and soil loss prediction, employing mass balance considerations of the surface 1 cm of soil. Below this depth, the pesticide is considered unavailable for runoff loss. Pesticide levels in the soil are also considered to decay exponentially with time. Meanwhile, total pesticide can be divided into adsorbed (solid-phase) and dissolved forms. The model can also allow for rainstorms subsequent to the first storm. To complete the pesticide runoff model, runoff and soil is also predicted, and is based partly on a modified Universal Soil Loss Equation (USLE) used to estimate soil loss from any rainfall event.

The model was tested (Haith, 1980) using data for atrazine losses for two small watersheds in Watkinsville, Georgia, applied as a surface spray to loosely tilled soil. Predicted and measured runoff, sediment, and atrazine losses for runoff-producing storms were presented. The accuracy of predictions varied among events showing that the model is not a suitable means of predicting losses from a single isolated storm. However, an estimation of average or seasonal losses are predicted fairly well. The total dissolved losses are more accurately predicted than solid-phase (adsorbed) losses.

d) An evaluation of some available pesticide runoff loading models.

Lorber and Mulkey (1982) tested three runoff models: ARM, Continuous Pesticide Simulation (CPS) and CREAMS, comparing them for their abilities to predict the movement of toxaphene and atrazine, using watershed studies in the Mississippi delta region. All the models accurately reproduced

field data. For the CPS and ARM models, predictions of total erosion differed from observations by 6%, whereas CREAMS underpredicted erosion by 25%. Model predictions of total runoff differed from field observations by 15% or less. All models were within 10% of observations of overland toxaphene loss predictions but their predictions of peak events did differ. ARM could predict higher losses of soluble chemicals than the other two, due to its unique interflow component. Similarly, CREAMS estimation of sediment enrichment resulted in higher toxaphene loss predictions than the other two.

1.9 Conclusion

Pesticide usage continues to increase in the U.K. so that concern with the possible effects on river catchments, especially on water quality will also continue. While the move away from the more persistent organochlorine pesticides is to be welcomed, the increasingly large quantities of OP's, pyrethroids and carbamates being applied need careful investigation with regard to their possible residue levels to be found in British rivers. Herbicides probably represent the area of most concern since their total applications dominate pesticide usage in the U.K., aerially and quantitatively.

Many factors influence the behaviour and fate of pesticides after contact with soil, including such factors as adsorption, leaching, volatilisation, erosion, microbial degradation, chemical degradation and hydrolysis. All of the above are in part dependent on soil characteristics as well as the chemical characteristics of the pesticide. Moreover, soil erosion in agricultural areas is a major process contributing pesticides to the aquatic environment. Other sources, however, include industrial and sewage effluent and accidental spillages. All of these factors and sources need to be taken into consideration in any general study of pesticides in catchments, and in any modelling exercise.

More specifically with regard to pesticides in rivers, the present E.E.C. drinking water standards appear hopelessly misguided and open to disregard since a global standard of 0.5 ug/l for the total pesticides present takes no account of the toxic nature of individual compounds. Certainly, this is the view of Thames W.A.

Recent studies both in Australia and North America, meanwhile, seem to indicate that the actual losses of pesticide rarely exceed 5% of the total,

applied, and as such are not alarming. However, what is of concern is the nature of the individual pesticide concentrations reaching rivers and their possible toxic effects on aquatic fauna. Clearly, storms following recent applications of pesticides represent the main period of concern since the changeover to less persistent pesticides.

The present water authority perspective on the possible pollution problems represented by pesticides varies. Thames W.A. experience "apparent" problems with the herbicides atrazine and simazine in relation to the levels present in supply waters. Yorkshire W.A., however, experience more urgent problems based on the industrial discharges of lindane in particular, from textiles maanufacturers, while Anglian W.A. have some evidence of elevated atrazine levels, probably due to indiscriminate urban usage.

Finally, with regard to the possibility of modelling pesticide movement within catchments, work in the U.S. suggests its feasilbility. Certainly, the ARM and CREAM models offer good examples, although they both have obvious limitations. All such models require hydrology, erosion and chemical components, if they are to successfully model pesticide losses. Data inputs to them also require in many instances, detailed field observations and careful calibration and validation. Such procedures would thus also be necessary for any model derived by the authors for the British context. It is hoped that the feasibility of designing such a model can be fully assessed by the end of the present contract.

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